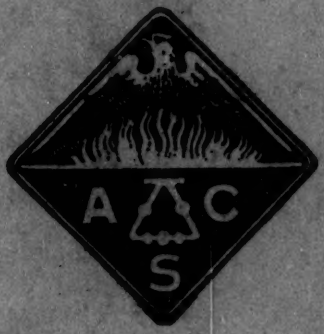
RUBBER CHEMISTRY AND TECHNOLOGY

VOLUME XXIV NUMBER 1



January-March, 1951

Published Quarterly under the Auspices of the
DIVISION OF RUBBER CHEMISTRY
of the
AMERICAN CHEMICAL SOCIETY
at Prince and Lemon Sts., Lancaster, Pa.

KOSMOS 60 RF

KOSMOS 60 RF

KOSMOS 60 RF

KOSMOS 60 RF

Kosmos 60 is today the most talked about furnace black for reinforcing natural and synthetic rubber. It originates from oil and is perfected by United's exclusive process. Its superb processing and balance of strength make for the best in rubber products.

UNITED CARBON COMPANY, INC.

CHARLESTON 27, W. VA.

NEW YORK • AKRON • CHICAGO • BOSTON

CANADA: CANADIAN INDUSTRIES LIMITED

CAN **WITCO**
ASSIST
WITH YOUR PROBLEMS?

our technicians are experts in:

the use of WITCO-made
- CARBON BLACKS
- METALLIC STEARATES
- WITCARB and WITCARB R
- PROCESSING AIDS
- M R (Hard Hydrocarbon)
- SUNOLITE (Anti-sunchecking wax)

So, to assist you in the many problems that today face the rubber compounder . . . shortage of natural rubber, increased prices of raw materials, availability of compounding ingredients . . . try

WITCO's TECHNICAL SERVICE

Whether it's conserving natural rubber, reformulating, or lowering costs, Witco's technical service staff is ready to put its experience to work for you. Write today.

WITCO CHEMICAL COMPANY

Continental Carbon Company

295 Madison Avenue • New York 17, N.Y.

Akron • Amarillo • Los Angeles • Boston • Chicago • Houston
Cleveland • San Francisco • London and Manchester, England

Entered as second-class matter March 19, 1943, at the Post Office at Lancaster, Pa., under the Act of August 24, 1912. Acceptance for mailing at special rate of postage provided for in paragraph (d-2), Section 34.40, P. L. and R. of 1948, authorized September 25, 1940.

See what **Philblack*** *can do for YOUR RUBBER PRODUCTS*

PHILBLACK A

The MAF black for better tire carcass and mechanical goods stocks . . . low heat buildup and excellent processing characteristics.

PHILBLACK O

The HAF black for tire treads . . . exceptionally high abrasion resistance and long flex life . . . particularly with "cold" rubber.

PHILLIPS CHEMICAL COMPANY

PHILBLACK SALES DIVISION

EVANS BUILDING · AKRON 8, OHIO

Phillips 66

Philblack A and Philblack O are manufactured at Borger, Texas.
Warehouses in Akron, Boston, Chicago, and Trenton
West Coast agent: Harwick Standard Chemical Company, Los Angeles
Canadian agent: H. L. Blachford, Ltd., Montreal and Toronto

*A Trademark

DOUBLE-CHECKED ✓ CHEMICALS FOR THE RUBBER INDUSTRY

THE "9" SERIES XTRUDED SHARPLES ACCELERATORS

For those who prefer extruded products, Sharples offers a line of ultra accelerators in this form. Other grades in powder form are also available from our plant and warehouses.

SA 52-9 TetraMETHYLthiuram DIsulfide
SA 57-9 ZINC diMETHYLdithiocarbamate
SA 62-9 TetraETHYLthiuram DIsulfide
SA 66-9 SELENIUM diETHYLdithiocarbamate
SA 67-9 ZINC diETHYLdithiocarbamate
SA 77-9 ZINC diBUTYLdithiocarbamate

For samples, prices and other information write Dept. R

SHARPLES CHEMICALS INC.

SHARPLES TRADE MARK CHEMICALS

SALES OFFICES:
350 FIFTH AVENUE, NEW YORK
34 CHERRY STREET, AKRON
80 E. JACKSON BLVD., CHICAGO

Thiokol*

SYNTHETIC RUBBERS and RUBBER CHEMICALS

CRUDES:

TYPE A — for stocks requiring unsurpassed solvent resistance.

TYPE FA — for extruded goods that must withstand aromatic blended fuels and permanent oil and weather-resistant putties.

TYPE PR-1 — for molded goods that must withstand aromatic blended fuels.

TYPE ST — for molded and extruded goods that must withstand aromatic blended fuels and low temperatures.

WATER DISPERSIONS:

MX & WD-6 — for liquid compounds to give films of high solvent and moisture resistance.

MF — for liquid compounds to give films of good solvent and low temperature resistance.

WD-2 — For liquid compounds to give films which must be free from odor. Films also have excellent low temperature resistance.

PLASTICIZERS:

TP-90B — for plasticizing natural rubber, GR-S, Buna N and GR-M for extreme low temperature resistance.

TP-95 — for plasticizing Buna N rubbers, GR-M and vinyl resins for excellent low temperature resistance and good heat resistance.

LIQUID POLYMERS:

LP-2 — A liquid polymer of 100% solids which vulcanizes to a tough resilient solid without shrinkage when mixed with curing agents.

LP-3 — same as LP-2 but of a lower viscosity.

TACKIFIERS:

GALEX W-100 & W-100D — A non-oxidizing rosin for imparting tack to the Buna rubbers. Also valuable in GR-M compounds.

TECHNICAL INFORMATION AND SAMPLES ON REQUEST

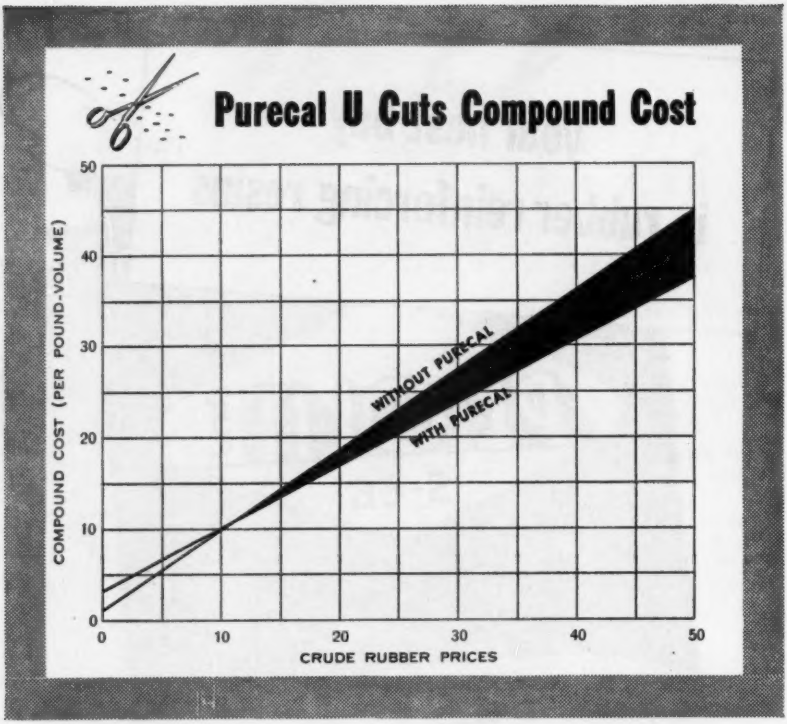
Thiokol CORPORATION
780 NORTH CLINTON AVENUE
TRENTON • NEW JERSEY

*THIOKOL, REG. U.S. PAT. OFF.

The Goodyear Tire & Rubber Company, Inc., Chemical Division, Akron 16, Ohio

We think you'll like "THE GREATEST STORY EVER TOLD"– Every Sunday – ABC Network

Pliolite—T. M. The Goodyear Tire & Rubber Company, Akron, Ohio



TAKE another look at that chart. It shows you exactly how much you save by using Purecal* U as an extender. You'll notice the savings begin at a fraction of a cent when crude rubber costs 11 cents per pound. You'll notice, too, that those savings can climb to three . . . four . . . five . . . even seven cents per pound-volume depending upon the price of crude rubber.

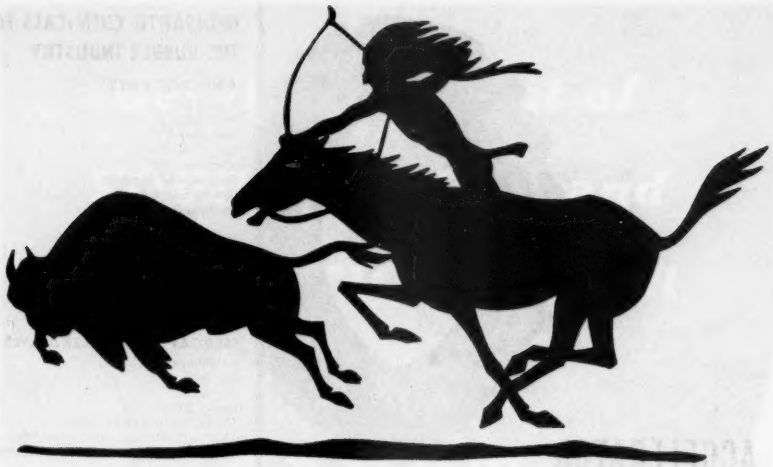
But that's only part of the story. In the formula on which this chart was based, Purecal U: (1) increased tear resistance 100%, (2) decreased curing time 75%, (3) maintained original "pure gum" tensile properties and hardness.

It will pay you to get acquainted with Purecal U. In this period of rising prices, the advantages of Purecal are bound to become more and more considerable. Write for the free booklet: "PURECAL IN NATURAL RUBBER." *Trade-mark

Soda Ash • Caustic Soda
Bicarbonate of Soda • Calcium Carbonate
Calcium Chloride • Chlorine
Hydrogen • Dry Ice • Synthetic Detergents
Glycols • Carbose (Sodium CMC)
Ethylene Dichloride • Propylene Dichloride
Aromatic Sulfonic Acid Derivatives
Other Organic and Inorganic Chemicals

WYANDOTTE CHEMICALS CORPORATION
Wyandotte, Michigan • Offices in Principal Cities

Wyandotte
REG. U. S. PAT. OFF.



... at close range

The closer the Indian got to his target, the surer he was that the arrow would strike accurately and with sufficient force.

You are closer to your "target" of quality production at the most economical cost when you depend upon ***TEXAS "E"*** and ***TEXAS "M"***, highest quality channel blacks.

With the world's largest channel black plant and available nearby natural resources, the Sid Richardson Carbon Co.,can assure you a continuous supply of these constantly uniform and economical-to-use blacks.

TEXAS
CHANNEL BLACKS

Sid Richardson
CARBON CO.
FORT WORTH, TEXAS

GENERAL SALES OFFICES
EVANS SAVINGS AND LOAN BUILDING
AKRON 8, OHIO

ACCELERATOR

For many kinds of compounds...

EL SIXTY

Whether you want an accelerator for surgical gloves or tractor tires, Monsanto's accelerator El Sixty will give you the performance you need.

El Sixty (Di [benzothiazyl thiomethyl] urea) offers these advantages:

Safe handling
Versatility
Good performance in white or colored stock
Ability to wade through retarding pigments
Excellent performance in pure gum or reclaim stock
Most stable accelerator in latex—causes no thickening in tanks
Can be used alone or activated with Guanidines, Aldehyde-amines, Thiurams or Dithiocarbamates

For complete information and experienced assistance in your rubber chemical problems, get in touch with MONSANTO CHEMICAL COMPANY, Rubber Service Department, 920 Brown Street, Akron 11, Ohio.

MONSANTO CHEMICALS FOR THE RUBBER INDUSTRY

ANTIOXIDANTS
Flectol H*
Santoflex* B
Santoflex BX
Santoflex 35
Santoflex AW
Santowhite* Crystals
Santowhite MK
Santowhite L

ALDEHYDE AMINE ACCELERATORS
A-32*
A-77*
A-100*

MERCAPTO ACCELERATORS
Santocure*
El-Sixty*
Ureka* C
Ureka Base
Mertax* (Purified Thiotax*)
Thiotax (2-Mercapto benzothiazole)
Thiofide* (2,2' dithio-bis benzothiazole)

GUANIDINE ACCELERATORS
Diphenyl Guanidine (D.P.G.)
Guantal*

ULTRA ACCELERATORS FOR LATEX, ETC.
R-2 Crystals*
Pip-Pip
Thiurad* (Tetra methyl thiuram disulfide)
Ethyl Thiurad (Tetra ethyl thiuram disulfide)
Mono Thiurad (Tetra methyl thiuram mono sulfide)
Methasan* (Zinc salt of dimethyl dithiocarbamic acid)
Ethasan* (Zinc salt of diethyl dithiocarbamic acid)
Butasan* (Zinc salt of dibutyl dithiocarbamic acid)

WETTING AGENTS AND DETERGENTS
Areskap* 50
Aresklene* 375
Santomerse* S
Santomerse D

SPECIAL MATERIALS
Thiocarbanilide ("A-1")
Santovar*-A
Santovar-O
Insoluble Sulfur "60"
Retarder ASA

COLORS

REODORANTS

*Reg. U. S. Pat. Off.

MONSANTO
CHEMICALS—PLASTICS

Serving Industry... Which Serves Mankind

Get the most out of

YOUR NATURAL and

SYNTHETIC RUBBER

with

CABOT

CARBON BLACKS

GODFREY L. CABOT, INC.

77 Franklin Street, Boston 10, Mass.

A LOW COST BUNA N PLASTICIZER

Excellent for **LIGHT COLORED PRODUCTS**

PANAFLEX BN-1

SPECIFY GRAVITY	0.9440
COLOR, NPA	1½
REFRACTIVE INDEX	1.553
DISTILLATION, °F	560-730
ODOR	Excellent
VISCOSITY, SSU @ 100°F	240

SAMPLES ON REQUEST

PANAFLEX BN-1 is an economical, light-colored plasticizer for synthetic rubber — especially butadiene-acrylonitrile type.

This hydrocarbon plasticizer *completely* replaces dibutyl phthalate in nitrile rubbers—produces soft vulcanizates having high tensile, excellent elongation, and very low modulus. **PANAFLEX BN-1** plasticized stocks possess good ageing properties, superior electrical characteristics, and show good gasoline and oil resistance.

PAN AMERICAN

PAN AMERICAN *Chemicals*
DIVISION
Pan American Refining Corp.
122 EAST 42nd STREET NEW YORK 17, N.Y.
Plant
Texas City, Texas

chemicals for the rubber industry

ACCELERATORS
- Thiazoles
  - MBT (Mercaptobenzothiazole)
  - MBTS (Benzothiazyldisulfide)
- Guanidine
  - DPG (Diphenylguanidine)
  - DOTG (Diorthotolylguanidine)
  - Accelerator 49

ACTIVATOR
- Aero* AC 50

ANTIOXIDANT
- Antioxidant 2246
  (Non-staining, non-discoloring type)

PEPTIZER
- Pepton® 22

RETARDER
- Calco Retarder P.D.

STIFFENING AGENT
- Calco S.A.

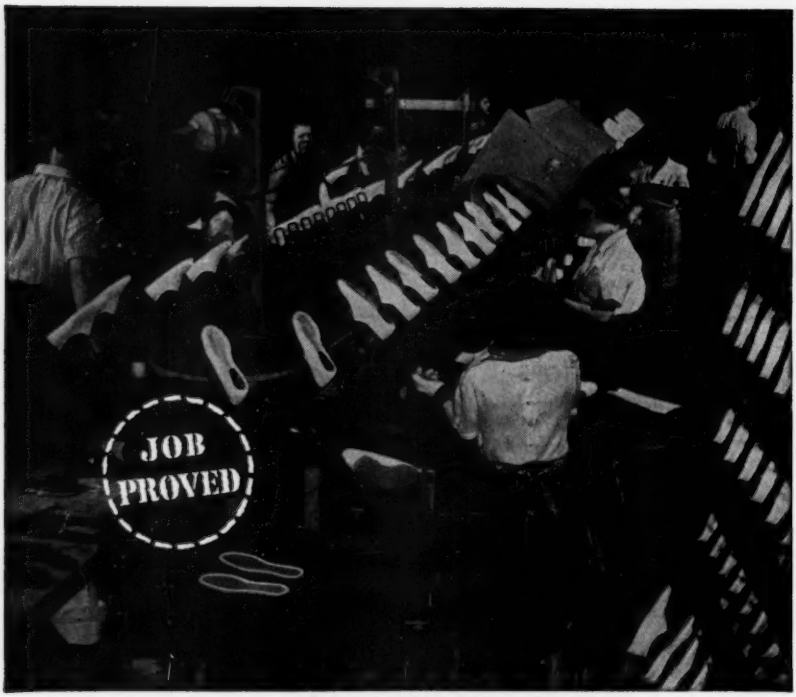
SULFUR
- Rubber Maker's Grade

*Trade-mark

Calco

AMERICAN Cyanamid COMPANY

CALCO CHEMICAL DIVISION
INTERMEDIATE & RUBBER CHEMICALS DEPARTMENT
BOUND BROOK, NEW JERSEY, U.S.A.



KEEPS WHITE FOOTWEAR WHITE

Sun Rubber-Process Aid Solves Costly Discoloration Problem

White rubber footwear discolored in use and colored sportswear soles bled into the white finishing tape. In trying to solve this serious problem, a large rubber manufacturer experimented with 12 specially selected process aids. Only two were successful: a Sun product and one much more expensive.

The Sun process aid was chosen and has proved completely satisfactory. Used to wet pigments, to soften rubber stocks, to smooth calendering, and to aid plasticizing, it causes neither staining nor discoloration. In fact, the white stocks treated with the Sun product retain their whiteness as long as control stocks containing no processing aid at all.

Sun rubber-process aids speed up milling and calendering; minimize bleeding and migrating; reduce flex-cracking, heat build-up, and hardening. Also they generally increase the resilience of the finished vulcanizate. Sun "Job Proved" process aids are refined for maximum compatibility with the types of rubber for which they are recommended —natural, synthetic, or reclaim.

To learn how Sun rubber-process aids may help you, call the nearest Sun Office. The services of a Sun representative are available without obligation.

SUN OIL COMPANY • *Phila. 3, Pa.*

In Canada: Sun Oil Company, Ltd.—Toronto and Montreal

SUN PETROLEUM PRODUCTS

"JOB PROVED" IN EVERY INDUSTRY

SUNOCO

RUBBER CHEMISTRY AND TECHNOLOGY

VOLUME XXIV NUMBER 1

January-March, 1951

Published under the Auspices of the
DIVISION OF RUBBER CHEMISTRY
of the
AMERICAN CHEMICAL SOCIETY

CARBON BLACKS

for **RUBBER COMPOUNDING**

•

MPC (Medium Processing Channel)
STANDARD MICRONEX

•

EPC (Easy Processing Channel)
MICRONEX W-6

•

HAF (High Abrasion Furnace)
STATEX-R

•

FF (Fine Furnace)
STATEX-B

•

FEF (Fast Extruding Furnace)
STATEX-M

•

HMF (High Modulus Furnace)
STATEX-93

•

SRF (Semi-Reinforcing Furnace)
FURNEX

• COLUMBIAN COLLOIDS •

COLUMBIAN CARBON CO. • **BINNEY & SMITH CO.**
MANUFACTURER DISTRIBUTOR

400 TONS OF SMOKE A DAY

RUBBER CHEMISTRY AND TECHNOLOGY

Published quarterly under the Auspices of the Division of Rubber Chemistry
of the American Chemical Society,
Prince and Lemon Streets,
Lancaster, Pa.

Editor ..... C. C. Davis
Advertising Manager ..... E. H. Krismann
Secretary ..... C. R. Haynes
Treasurer ..... A. W. Oakleaf

Vol. XXIV **Jan.-Mar., 1951** **No. 1**

CONTENTS

General Section PAGE

Officers iii
Fall Meeting of the Division of Rubber Chemistry vi
New Books and Other Publications ix

Papers

Light Stiffening of Rubber. R. G. Newton and W. C. Wake 1
The Oxidation of Rubber Vulcanizates. Holger Leth Pedersen 18
Alfin Catalysts and the Polymerization of Butadiene. Avery A. Morton 35
Theory on the Crystallization and Melting of Unvulcanized Rubber. I. Crystallization. Ryoichi Kikuchi 54
Theory on the Crystallization and Melting of Unvulcanized Rubber. II. Melting. Ryoichi Kikuchi 64
Stress-Strain Properties of Natural Rubber Under Biaxial Strain. B. B. S. T. Boonstra 70
Equivalent Effects of Time and Temperature in the Shear Creep and Recovery of Elastomers. F. S. Conant, G. L. Hall, and W. James Lyons 83
The Structure of Elastomers and Their Reactivity. A. S. Kuz'minskiĭ and N. H. Lezhnev 95
The Role of Intermolecular Forces in the Mechanism of High Elastic Deformation. II. Relaxation Properties of Natural Rubber and Its Bromination Products. B. Dogadkin and M. Reznikovskiĭ 99
Influence of Structure of Elastomers on Their Permeability to Gasses. G. J. Van Amerongen 109
Equation of State of Rubber From the Viewpoint of Thermodynamics. G. M. Bartenev 132
Change in the Relaxation Properties of Vulcanized Rubber on Swelling. A. Dogadkin and V. E. Gul 140

Ultra-Speed Tensile of Rubber and Synthetic Elastomers. D. S. Villars..... 144

The Mechanism of the Action of Aromatic Thiols on Rubber Solutions. E. P. Kheraskova and A. P. Gamayunova..... 161

Crystal Violet, An Electronic Model Substance for Rubber and Related Olefins. G. J. Van Veersen..... 169

Birefringence of Rubbers. D. W. Saunders..... 182

Partially Chlorinated Derivatives of Rubber. D. E. Woods..... 184

The Preparation of Cyclized Rubber From Natural-Rubber Latex. G. J. Van Veersen..... 195

Polar Rubbers and Their Application as Ion Exchangers. Pierre Mastagli, Geza Austerweil, and Azfiri Zafiriadis..... 197

Impact Resilience as a Function of Temperature. B. B. S. T. Boonstra..... 199

Organic Sulfides as Vulcanizing Agents of Rubber. R. L. Sibley..... 211

Determination of Free Carbon in Cured Rubber Stocks. I. M. Kolthoff and R. G. Gutmacher..... 224

RUBBER CHEMISTRY AND TECHNOLOGY

Rubber Chemistry and Technology is published quarterly under the supervision of the Editor representing the Division of Rubber Chemistry of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

Rubber Chemistry and Technology may be obtained in one of three ways:

(1) Any member of the American Chemical Society may become a member of the Division of Rubber Chemistry by payment of the dues ($2.50 per year) to the Division and thus receive Rubber Chemistry and Technology.

(2) Anyone who is not a member of the American Chemical Society may become an Associate of the Division of Rubber Chemistry upon payment of $5.00 per year to the Treasurer of the Division of Rubber Chemistry, and thus receive Rubber Chemistry and Technology.

(3) Companies and libraries may subscribe to Rubber Chemistry and Technology at the subscription price of $5.00 per year.

To these charges of $2.50 and $5.00, respectively, per year, postage of $.20 per year must be added for subscribers in Canada, and $.50 per year for those in all other countries not United States possessions.

All applications for regular or for associate membership in the Division of Rubber Chemistry with the privilege of receiving this publication, all correspondence about subscriptions, back numbers, changes of address, missing numbers, and all other information or questions should be directed to the Treasurer of the Division of Rubber Chemistry, A. W. Oakleaf, Phillips Chemical Co., 605 Evans Building, Akron 8, Ohio.

Articles, including translations and their illustrations, may be reprinted if due credit is given Rubber Chemistry and Technology.

THE DIVISION OF RUBBER CHEMISTRY OF THE AMERICAN CHEMICAL SOCIETY

OFFICERS AND EXECUTIVE COMMITTEE

Chairman.....J. H. Fielding, Armstrong Rubber Co., West Haven, Conn.
Vice-Chairman.....W. L. Semon, B. F. Goodrich Research Center, Brecksville, Ohio
Secretary.....C. R. Haynes, Binney & Smith Co., New York, N. Y.
Treasurer.....A. W. Oakleaf, Phillips Chemical Co., Akron, Ohio
Editor of *Rubber Chemistry & Technology*.....C. C. Davis, Boston Woven Hose & Rubber Co., Cambridge, Mass.
Advertising Manager of *Rubber Chemistry & Technology*....E. H. Krismann, E. I. du Pont de Nemours & Co., Akron, Ohio
Directors....F. W. Stavely (Past Chairman), W. J. Sparks (Director-at-Large), C. C. Davis, E. H. Krismann; (regional group representatives for two years), H. F. Palmer (Akron), J. C. Walton (Boston), E. C. Siverson (Buffalo), F. S. Frost, Jr. (Chicago), R. E. Bitter (Los Angeles), M. R. Buffington (New York); (regional group representatives for one year), W. J. O'Brien (Connecticut), G. P. Hollingsworth (Detroit), G. S. Ramsey (Northern California), R. A. Kurtz (Philadelphia), E. L. Hanna (Rhode Island), R. A. Clark (Southern Ohio), Norman Bekkedahl (Washington, D. C.)

COUNCILLORS

H. E. Outcault, F. W. Stavely (*Alternates*, A. M. Neal, J. C. Walton)

COMMITTEES

Auditing—R. D. Juve (Chairman), W. H. Ayscue, V. K. Hitch.
Bibliography—J. McGavack (Chairman), C. C. Davis, M. E. Lerner, C. W. Christensen, V. L. Burger, D. E. Cable, T. L. Wilson.
Dues—L. V. Cooper (Chairman), H. I. Cramer, S. G. Byam, A. W. Oakleaf.
Files and Records—J. D. D'Ianni (Chairman), A. M. Neal, R. B. Appleby, Dorothy Hamlen.
Finance and Budget—J. M. Bierer (Chairman), J. W. Temple, N. A. Shepard.
Goodyear Medal—F. W. Stavely (Chairman).
Liaison—W. L. Semon (Chairman), R. E. Hutchinson, A. E. Laurence, H. W. Sutton, T. A. Werkenthin.
Library—B. S. Garvey, Jr. (Chairman), Fern Bloom, Lois Brock, Dorris Hall, Dorothy Hamlen, H. E. Simmons, H. N. Stevens, Leora Straka, H. C. Tingey, R. B. Appleby.
Membership—J. F. Kerscher (Chairman). *Akron.*—M. J. Sanger. *Boston.*—J. L. Haas. *Buffalo.*—A. H. Davis. *Chicago.*—F. S. Frost, Jr. *Connecticut.*—E. W. Schwartz. *Detroit.*—G. R. Cuthbertson. *Los Angeles.*—G. W. Miller. *New York.*—G. N. Vacca. *Northern California.*—G. S. Ramsey. *Philadelphia.*—James Johnson. *Rhode*

Island.—F. H. SPRINGER. *Southern Ohio.*—J. E. FELDMAN. *Washington.*—J. T. COX.

Nominating—J. N. STREET (Chairman), J. T. BLAKE, H. E. OUTCAULT, G. C. MAASSEN, R. G. SEAMAN.

Papers Review—C. R. HAYNES, C. C. DAVIS, W. L. SEMON.

Symposium—G. R. CUTHBERTSON, J. D. D'IANNI, A. E. JUVE, J. W. LISKA, W. B. REYNOLDS, L. A. WOHLER.

Tellers—J. W. SNYDER (Chairman), M. E. LERNER, S. M. MARTIN.

OFFICERS OF LOCAL GROUPS

AKRON

Chairman....E. L. STANGOR (E. I. du Pont de Nemours & Co., Akron). *Vice-Chairman*....D. F. BEHNEY (Harwick Standard Chemical Co., Akron). *Secretary*....L. M. BAKER (General Tire & Rubber Co., Akron 9). *Treasurer*....R. D. JUVE (Mohawk Rubber Co., Akron). (Terms expire September 1, 1951.)

BOSTON

Chairman....T. C. EDWARDS (Acushnet Process Co., New Bedford, Mass.). *Vice-Chairman*....JOHN ANDREWS (Godfrey L. Cabot, Inc., Boston). *Secretary-Treasurer*....A. W. BRYANT (Binney & Smith Co., Boston). (Terms expire December 31, 1951.)

BUFFALO

Chairman....P. J. SICK (Hewitt-Robins, Inc., Buffalo). *Vice-Chairman*....F. A. KOHLHAGEN (Globe Woven Belting Co., Buffalo). *Secretary-Treasurer*....R. J. LOWRY (Hewitt-Robins, Inc., Buffalo). (Terms expire December 31, 1951.)

CHICAGO

Chairman....P. F. NIESSEN (Victor Manufacturing & Gasket Co., Chicago). *Vice-Chairman*....J. F. TAYLOR (Commercial Solvents Corp., Chicago). *Secretary-Treasurer*....J. E. A. HOPKINS (Van Cleef Brothers, Chicago). (Terms expire April 20, 1951.)

CONNECTICUT

Chairman....C. A. LARSON (Whitney Blake Co., Hamden, Conn.). *Vice-Chairman*....G. R. SPRAGUE (Sponge Rubber Products Co., Derby, Conn.). *Secretary*....G. A. DI NORSCIA (Sponge Rubber Products Co., Derby, Conn.). *Treasurer*....F. J. ROONEY (General Electric Co., Bridgeport, Conn.). (Terms expire December 31, 1951.)

DETROIT

Chairman....G. F. LINDNER (Minnesota Mining & Manufacturing Co., Detroit). *Vice-Chairman*....G. R. CUTHBERTSON (U. S. Rubber Co., Detroit). *Secretary*....G. P. HOLLINGSWORTH (Minnesota Mining & Manufacturing Co., Detroit). *Treasurer*....E. V. HINDLE (U. S. Rubber Co., Detroit). (Terms expire December 31, 1951).

Los Angeles

Chairman....R. D. Abbott (R. D. Abbott Co., Los Angeles). *Associate Chairman*....R. L. Short (Kirkhill Rubber Co., Los Angeles). *Vice-Chairman*....D. C. Maddy (Harwick Standard Chemical Co., Los Angeles). *Secretary*....F. C. Johnston (Caram Manufacturing Co., Monrovia, Calif.). *Treasurer*....C. S. Hoglund (R. D. Abbott Co., Los Angeles). (Terms expire December 31, 1951).

New York

Chairman....M. R. Buffington (Lea Fabrics, Inc., Newark, N. J.). *Vice-Chairman*....J. S. Corrigall (R. T. Vanderbilt Co., New York). *Secretary-Treasurer*....B. B. Wilson (*India Rubber World*, New York). (Terms expire December 31, 1951.)

Northern California

Chairman....J. B. Watson (Goodyear Rubber Co., San Francisco). *Vice-Chairman*....Neil McIntyre (Oliver Tire and Rubber Co., Oakland.) *Secretary*....Grover Ramsey (Grove Regulator Co., Oakland). *Treasurer*.... James Sanford (American Rubber Co., Oakland). (Terms expire December 31, 1951.)

Philadelphia

Chairman....H. J. Reid (Gilmer Division, U. S. Rubber Co., Philadelphia). *Vice-Chairman*....T. W. Elkin (Armstrong Cork Co., Lancaster, Pa.). *Secretary-Treasurer*....George Wyrough (R. E. Carroll Co., Trenton). (Terms expire at meeting in January 1952).

Rhode Island

Chairman....F. V. Newman (Respro, Inc., Cranston, R. I.). *Vice-Chairman*....C. L. Kingsford (Davol Rubber Co., Providence). *Secretary-Treasurer*....R. G. Volkman (U. S. Rubber Co., Providence). (Terms expire at Fall meeting of 1951.)

Southern Ohio

Chairman....L. J. Keyes (Dayton Rubber Co., Dayton). *Vice-Chairman*....J. E. Feldman (Inland Manufacturing Division, General Motors Corp., Dayton). *Secretary*....R. J. Hoskin (Inland Manufacturing Div., General Motors Corp., Dayton). (Terms expire December 31, 1951.)

Washington, D. C.

Chairman....Warren Stubblebine (Office of the Quartermaster-General, Dept. of the Army, Washington). *Vice-Chairman*....T. R. Scanlan (Gates Rubber Co., Washington). *Secretary*....R. E. Harmon (Connecticut Hard Rubber Co., Washington). *Treasurer*....E. G. Holt (Office of Domestic Commerce, U. S. Dept. of Commerce, Washington). *Recording Secretary*.... (Miss) Ethel Levene (Bureau of Ships, U. S. Navy Dept., Washington). (Terms expire October, 1951.)

FALL MEETING OF THE DIVISION OF RUBBER CHEMISTRY CLEVELAND, OHIO, OCTOBER 11–13, 1950

The 57th meeting of the Division of Rubber Chemistry was held in Cleveland on October 11–13, under the Chairmanship of F. W. Stavely. This was an "International Meeting" and the Division was favored by the presence of more than 50 leading chemists and technologists from overseas.

The Division headquarters was at the Hotel Cleveland, and the Suppliers' cocktail party and the banquet were held at the Hotel Carter. Local arrangements were in the hands of a committee headed by Amos W. Oakleaf, general chairman, and the following: C. A. Smith, Vice-Chairman; F. A. Bonstedt, Banquet; C. W. Christensen, Advisory; C. A. Hemingway, Foreign Liaison; E. H. Krismann, Registration; H. F. Palmer, Treasurer; W. von Fischer, Meeting Rooms; R. F. Wolf, Publicity.

The Suppliers' cocktail party was ably handled by J. M. Hamilton and A. I. Brandt.

1138 members and guests registered for the meeting, an attendance which has been exceeded but once. The attendance at the banquet was slightly over 1000.

R. P. Dinsmore presided over the meeting of the 25-Year Club, which 165 members and guests from overseas attended.

The Directors held two meetings and the Division held a Business Meeting. At the Business Meeting the Chairman notified the members of the death of two of our members: James J. Boyle of Rubber & Plastics Section, Fort Belvoir, Va., and J. E. Whittenberg, Firestone Tire & Rubber Co., Akron, Ohio.

L. V. Cooper reported the membership to be 2725, of whom 343 are associate members. A. R. Davis of the Ballot Committee reported that 935 ballots had been cast and that, in addition to the Chairman, Secretary, and Treasurer, which were uncontested offices, the following were elected:

Vice-Chairman, Waldo L. Semon; Director-at-Large, W. J. Sparks. *Directors for two-year terms:* H. F. Palmer (Akron); J. C. Walton (Boston); E. C. Siverson (Buffalo); F. S. Frost, Jr. (Chicago); R. E. Bitter (Los Angeles); M. R. Buffington (New York). *Directors for one-year terms:* W. J. O'Brien (Connecticut); G. P. Hollingsworth (Detroit); G. S. Ramsey (No. California); R. A. Kurtz (Philadelphia); E. L. Hanna (Rhode Island); R. A. Clark (Southern Ohio); Norman Bekkedahl (Washington, D. C.).

J. H. Fielding is the new Chairman.

One of the features of the meeting was the presentation of the seventh Charles Goodyear Address by C. C. Davis of the Boston Woven Hose & Rubber Co., and Editor of *Rubber Chemistry & Technology*. Mr. Davis' subject was "Some of the Real Pioneers of the Rubber Industry," and his well documented talk was listened to with great interest.

The program at the banquet included: Introductory remarks by Chairman F. W. Stavely; Greetings to Overseas Guests by R. P. Dinsmore; Response by W. J. S. Naunton; Review of the Activities of our Medalist by J. C. Walton; Presentation of Medalist to the Chairman by H. I. Cramer; Presentation of the Medal by Chairman, F. W. Stavely, and Entertainment.

The number of papers was so great that it was necessary for the first time at any meeting to hold concurrent sessions on two of the half-day periods. Vice-Chairman Fielding presided over one of these concurrent sessions, and Chairman Stavely over the other.

The following papers were presented:

Vulcanization Characteristics of N,N′-Dithioamines in Furnace Black Stocks. M. C. Throdahl and M. W. Harman (Monsanto Chemical Co., Nitro, W. Va.).

Bonding of Butyl Rubber to Brass. R. W. Kaercher and G. W. Blum (Case Institute of Technology, Cleveland).

Aging of Black Neoprene Jackets. G. N. Vacca, R. H. Erickson and C. V. Lundberg (Bell Telephone Laboratories, Murray Hill, N. J.).

Effect of Synthetic Elastomers on the Properties of Petroleum Asphalts. H. A. Endres, R. J. Coleman, R. M. Pierson, and E. A. Sinclair (Goodyear Tire & Rubber Co., Akron).

Influence of particle size on creaming of rubber latex by means of ammonium alginate. E. Schmidt and R. H. Kelsey (Firestone Tire & Rubber Co., Akron).

Direct Reënforcement of Natural Rubber Latex Mixtures. J. Le Bras and I. Piccini (French Rubber Institute, Paris).

Influence of Soaps on the Gelling Characteristics of Hevea Latexes. D. J. McKeand (Dunlop Rubber Co., London, England).

The Zinc Oxide Stability of Latex. G. E. van Gils (Indonesian Rubber Research Institute, Bogor).

Absorption of Oxygen by Ammonia-Preserved Latex. J. McGavack and E. M. Bevilacqua (United States Rubber Co., Passaic, N. J.).

Kinetics of Cyclization of Hevea Latex. M. Gordon (Dunlop Rubber Co., Birmingham, England).

Presence of an Esterase in Latex of Hevea Brasiliensis. L. N. S. de Haan-Homans (Indonesian Rubber Research Institute, Bogor).

Determination of the Molecular Structure of Rubbers by Physical Methods. L. Nielsen, R. Buchdahl, and G. Claver (Monsanto Chemical Co., Springfield, Mass.).

Influence of Fillers on the Elastic Modulus and Swelling of Butyl Networks. R. L. Zapp (Esso Laboratories, Linden, N. J.) and E. Guth (University of Notre Dame, Notre Dame, Indiana).

Some Optical Examinations of Anistropy in Vulcanizates. Stefano Oberto (Società Pirelli per Azioni, Milan, Italy).

Inflation of a Rubber Diaphragm. J. E. Adkins and R. S. Rivlin (British Rubber Producers' Research Association, Welwyn Garden City, England).

Study of Bonded Units. J. M. Buist and W. J. S. Naunton (Imperial Chemical Industrial, Ltd., Manchester, England).

The Goodyear Lecture. Some of the Real Pioneers of the Rubber Industry. C. C. Davis. (Editor of *Rubber Chemistry & Technology*).

Butadiene-Styrene Resinous Copoloymers. J. D. D'Ianni, L. D. Hess, and W. C. Mast (Goodyear Tire & Rubber Co., Akron).

Plastics from Natural Rubber. G. Salomon, G. J. van Amerongen, G. J. van Veersen, G. Schuur, and H. C. J. de Decker (Rubber Foundation, Delft, Holland).

Reënforcement of Rubber. R. Houwink (Rubber Foundation, Delft, Holland).

Dynamic Study of Reënforcement. J. R. S. Waring (Imperial Chemical Industries, Ltd., Manchester, England).

Improvements in Accuracy of Hardness Testing. J. R. Scott (Research Association of British Rubber Manufacturers, Croydon, England).

Hysteresis of Vulcanized Rubber for Small Elongations. P. THIRION AND J. MARTIN (French Rubber Institute, Paris).

Retraction Test for Serviceability of Elastomers at Low Temperatures. O. H. SMITH, W. A. HERMONAT, H. E. HAXO, AND A. W. MEYER (United States Rubber Co., Passaic, N. J.).

Use of Inclined-plane Tester to Determine Intrinsic Low Stress Properties of Rubber Compounds. W. B. DUNLAP, JR., C. J. GLASER, JR., AND A. H. NELLEN (Lee Rubber & Tire Co., Conshohocken, Pa.).

Ultraviolet Spectrophotometric Analysis of Organic Rubber Accelerator Masterbatch Stocks. K. E. KRESS (Firestone Tire & Rubber Co., Akron).

Polysulfide Liquid Polymers. A New Type of Vulcanizable Liquid Rubbers. J. S. JORCZAK AND E. M. FETTES (Thiokol Corp., Trenton, N. J.).

Adhesion of Rubber and Textiles. V. Effect on Adhesion of the Amount of Spun Staple Yarn in the Fabric. E. M. BORROFF AND W. C. WAKE (Research Association of British Rubber Manufacturers, Croydon, England).

Some Problems Involved in the Grading and Testing of Natural Rubber. III. Relation Between Compound Viscosity and Vulcanizate Stiffness. R. F. BLACKWELL, C. M. BLOW, AND W. P. FLETCHER (British Rubber Producers' Research Association, Welwyn Garden City, England).

Definition and Measurement of Rate of Cure. G. GEE (British Rubber Producers' Research Association, Welwyn Garden City, England).

Tackiness of Masticated and Compound Rubber Mixes. A. VAN ROSSEM AND J. M. VERCRUIJSSE (Rubber Research Institute, T. N. O., Delft, Holland).

Cis- and Trans-Polyisoprenes from a Single Plant Species. W. SCHLESINGER AND H. M. LEEPER (Wm. Wrigley Co., Chicago).

Aspects of the Problem of Obtaining Uniform Malayan Rubber. R. G. NEWTON, M. W. PHILPOTT, H. FAIRFIELD-SMITH, AND W. G. WREN (Rubber Research Institute of Malaya, Kuala Lumpur).

Some Aspects of Peroxide Decomposition and its Relation to Rubber Degradation. C. E. KENDALL (Dunlop Rubber Co., Brimingham, England).

Permanganate Oxidation of Polybutadiene Rubbers, F. J. NAPLES AND J. D. D'IANNI (Goodyear Tire & Rubber Co., Akron).

Contribution to the Study of Rubber Oxidation and Antioxidant Action. S. BAXTER, W. McG. MORGAN, AND D. S. P. ROEBUCK (Monsanto Chemicals, Ltd., London, England).

Deterioration of Rubber Under the Influence of Light and of Dry and Moist Heat. A. L. SODEN AND W. C. WAKE (Research Association of British Rubber Manufacturers, Croydon, England).

Factors Influencing the Creep and Stiffness of Vulcanized Rubbers. D. H. COOPER (Dunlop Rubber Co., Birmingham, England).

Rheometric Tests and Extrusion. S. ECCHER (Società Pirelli per Azioni, Milan, Italy).

Safe Limits of Sample Thickness for Rubber Oxidation and Aging Studies. G. W. BLUM, J. R. SHELTON AND H. WINN (Case Institute of Technology, Cleveland).

Evaluation of a Volumetric Oxygen Absorption Test for Rubber Aging. J. R. SHELTON AND W. L. COX (Case Institute of Technology, Cleveland).

Degree of Crystallization of Vulcanized Rubber as Calculated from the Temperature Coefficient of the Elastic Tension. B. B. S. T. BOONSTRA (Rubber Foundation, Delft, Holland).

Applications of spectroscopy to vulcanization studies. H. P. KOCH (British Rubber Producers' Research Association, Welwyn Garden City, England).

Dynamic properties of raw and vulcanized polymers. R. S. Enabnit and S. D. Gehman (Goodyear Tire and Rubber Co., Akron).

Crystallinity of high polymers. H. N. Carpenter Campbell and M. D. Allen (United States Rubber Co., Passaic, N. J.).

C. R. Haynes, *Secretary*

NEW BOOKS AND OTHER PUBLICATIONS

International Rubber Statistics. By W. G. G. Kellett. Royal Statistical Society, 4 Portugal Street, London, W. C. 2, England. $6\frac{3}{4} \times 9\frac{1}{4}$ in. 18 pp. 25c.—The information contained in this booklet has been reprinted from material which originally appeared in the *Journal of the Royal Statistical Society*. The booklet deals with the statistics of the raw material and not with the various products manufactured from rubber. Principally, the booklet concerns itself with world statistical information on natural and synthetic rubber and touches lightly on reclaimed rubber. Such matters as acreage, yields per acre, seasonal variations in rubber production, productive capacities, production of synthetic latices, and much other pertinent and interesting data are presented. [From *The Rubber Age* of New York.]

Annuaire de L'Industrie du Caoutchouc et de Ses Dérivés. 1950 (Third) Edition. Camille Rousset. Distributed by l'Institut Français du Caoutchouc, 42 Rue Scheffer, Paris XVI, France. Hard cover, 312 pages, $6\frac{1}{4}$ by $9\frac{1}{2}$ inches.—The present edition of this directory of the rubber and allied industries—which, we may add, the Institute Français du Caoutchouc supplies on request for only the cost of the postage—is divided into two sections. In the first part are listed, in alphabetical order and in separate sections, the names of manufacturers, dealers, importers of rubber, rubber plantation companies, and suppliers of machinery, chemical products, raw materials, and the miscellaneous requirements of the rubber industry. Under the heading, manufacturers of rubber, are also included for the first time lists of foreign rubber manufacturers, and we find besides the 30 odd pages of French firms, about six pages of British firms, five pages of Italian firms, and 22 of American concerns; in addition appear the names of 21 companies in Belgium, 18 in the Saar territory, and 37 in Switzerland.

In the second part (for French firms only) the classification is by products, also alphabetically arranged.

The directory proper is preceded by about 30 pages of information about the constitution, function, and membership of various organizations, including the Institut Français du Caoutchouc, the Union des Planteurs de Caoutchouc, the Syndicat du Caoutchouc, the Syndicat Général des Commerces et Industries du Caoutchouc, and associations representing the tire industry and dealers in tires and general rubber goods. [From the *India Rubber World.*]

Rubber Trade Directory of Great Britain: 1950. Published by Maclaren and Sons, Ltd., Stafford House, Norfolk St., London W. C. 2, England. $6 \times 9\frac{1}{2}$ in. 752 pp. £3 3s. Od. ($9.00 in the United States and Canada).—This is the first edition of a long-awaited and long-needed complete directory of the rubber industry of Great Britain. Patterned along the lines of the *Rubber Red Book*, it is designed to fulfill both the requirements of the rubber manufacturer in his daily search for rubber chemicals and compounding ingredients, machinery and equipment, raw material supplies, etc., and the vast

army of users of rubber products in all of their numerous shapes and forms. The publishers plan on issuing revised editions every other year.

Shaped to the special requirements of the British Rubber industry, the contents of the directory appear in English, French, German, and Spanish. A comprehensive subject index at the back of the directory, covering 87 pages, is also repeated in the three foreign languages, with the English translation given after each entry. Since the British industry depends in large part on the export trade, this treatment considerably enchances the value of the work.

The edition is divided into 15 sections, as follows: (1) Rubber Manufacturers; (2) Rubber Machinery and Equipment; (3) Instrument and Laboratory Equipment; (4) Chemicals and Compounding Ingredients; (5) Fabrics and Textiles; (6) Components; (7) Natural Rubber and Latices; (8) Synthetic Rubbers, Latices and Kindred Materials; (9) Reclaimed Rubbers; (10) Scrap and Waste Rubber Merchants; (11) Manufacturers' Sundry Requirements; (12) Trade Marks and Brand Names; (13) Trade and Research Organizations; (14) Rubber Technology Schools and Courses; (15) Who's Who in the British Rubber Industry. In addition, appendices give data on overseas agents and offices and on consultants.

The first edition of this new biennial directory of the British rubber industry leaves little to be desired, and the publishers will find improvement difficult. It is excellently printed on good white coated paper, with divider strips setting off each section. Liberal use has been made of bold-face type, with the result that listings stand out prominently. The publishers are to be congratulated for a difficult job well done. [From *The Rubber Age* of New York.]

SUMMARY OF THE REPORT OF THE DIRECTOR OF RESEARCH, 1949. By Geoffrey Gee. British Rubber Producers' Research Association, Inc., 19 Fenchurch St., London E. C. 3, England. 12 pages.—This report discusses the objectives of the Association's laboratory work, and lists and describes the main research and development projects conducted in 1949 and 1950. [From the *India Rubber World.*]

MARKETING AND UTILIZATION OF RUBBER LATEX IN INDIA. (Special Pamphlet No. 4). The Indian Rubber Board. Travancore, South India. $7\frac{1}{4} \times 9\frac{3}{4}$ in. 24 pp.—This pamphlet offers a compilation of material on the rubber latex industry in India. The rise of the industry since 1934 is described, and latex as a raw material and in its preparation for market are discussed. The marketing of both normal and concentrated latex is outlined, with special attention to sampling and containers and tanks. The properties of concentrated latex and advantages to be derived from its use are presented. The section of the pamphlet on the utilization of latex is illustrated with many photographs which depict the various uses to which the latex has been put. Other factors in the pamphlet are price data and information on developments. A valuable appendix and index complete this informative pamphlet. [From *The Rubber Age* of New York.]

A SURVEY OF AUTOMOTIVE ENGINEERS IN REGARD TO NATURAL AND SYNTHETIC RUBBER IN PASSENGER CAR TIRES. Natural Rubber Bureau, 1631 K St., N.W., Washington, 6 D. C. $8\frac{1}{2} \times 11$ in. 32 pp.—The results of a survey designed to secure accurate and objective information on the relative merits of natural and synthetic rubber for passenger-car tires are given. It

reflects the opinions of 32 automotive engineers, all of whom were asked to agree or disagree with nine specific statements. When asked to take all factors into consideration, 18 (or 56 per cent) expressed their preference for a 100 per cent natural rubber tire; 8 (or 25 per cent) preferred a synthetic rubber tire with a substantial increase in the present natural rubber content, 4 (or 12½ per cent) chose a synthetic tire built to present government specifications, and 2 (or 6½ per cent) expressed no preference. The statements, a tabulation of the replies, and various comments are given in the report. [From *The Rubber Age* of New York.]

ASPECTS OF RUBBER IN ENGINEERING. Institution of the Rubber Industry, 12 Whitehall, London, S.W. 1, England. 5½ × 8½ in. 96 pp. Approximately 50 c.—Six papers, originally presented at the London Section Conference held on March 17, 1950, are presented in this booklet. The papers presented include: "Factors Operating in the Measurement of the Dynamic Properties of Rubber," by W. P. Fletcher and A. N. Gent; "Measurements of the Dynamic Elasticity of Rubber", by K. W. Hillier; "Influence of Design on Rubber Springs", by A. E. Moulton and P. W. Turner; "Aspects of the Measurement of the Dynamic Properties of Rubber", by L. Mullins; "Some Theoretical Aspects of Dynamical Experiments on Rubber", by R. S. Rivlin, and "Dynamic Testing in Compression", by J. S. Waring. [From *The Rubber Age* of New York.]

RUBBER FOR THE ABSORPTION OF VIBRATION. By J. F. Downie Smith. Published by the Iowa Engineering Experiment Station. Iowa State College, Ames, Iowa. 8½ × 11 in. 50 pp.—This booklet, virtually a manual on the application of rubber for the absorption of vibration, contains five papers prepared by the author and previously published in various scientific journals, and one hitherto unpublished paper. Titles of the papers are as follows: (1) Rubber Mountings; (2) Rubber Springs—Shear Loading—I; (3) Rubber Springs—Shear Loading—II; (4) Rubber Springs Under Compression Loading; (5) Research on Rubber for Mechanical Engineers; (6) The Design of Rubber Mountings. The latter paper is the one now published for the first time. [From *The Rubber Age* of New York.]

COLLOID SCIENCE. By James W. McBain, D. C. Heath & Co., 285 Columbus Ave., Boston 16, Mass. Trade edition distributed by Reinhold Publishing Corp., 330 W. 42nd St., New York 18, N. Y. Cloth, 6 by 9¼ inches, 462 pages. Price: trade edition, $8.00; text edition, $6.00.—Designed to give a clear picture of colloid science, its scope and basic principles, this volume will be of great value to graduate students and workers in the field. For those unacquainted with the subject, the book leaves much to be desired. There is little mention of the history of colloid science; no comprehensive discussion of the colloidal state as such appears, nor is there anything on terminology. On the other hand, some of the chapters are extremely well presented, and in all cases the text is clearly and simply written, with many illustrations to clarify and enhance the discussion.

The scope of the book, and also that of the field of colloid science, can be seen by the subject matter of the chapters: emulsions and foam; sorption; effective depth of surfaces; preparation of colloidal sols; optical properties and study of colloids; Brownian movement; ultrafiltration; lyotropic series of ions;

viscosity, thixotropy, and plasticity and dilitancy; jellies and gels; coagulation, protective action, and sensitization; electrical and electrokinetic phenomena; diffusion; osmotic pressure and membrane equilibrium; ultracentrifuges and centrifuges; soaps and other colloidal electrolytes; solutions of proteins; nonaqueous systems of colloids; x-ray and other methods of studying colloids and high polymers; cellulose and its derivatives; other natural polysaccharides; natural and synthetic rubber; silk, wool, keratin, collagen, and the globular proteins; artificial polymers; resins, and plastics; clay; and aerosols. In addition to the usual author and subject indices, an index of chemicals and compounds is also included. [From the *India Rubber World.*]

COLLOIDAL DISPERSIONS. By Earl K. Fischer. Published by John Wiley & Sons, Inc., 440 Fourth Ave., New York 16, N. Y. (October 1950). $6 \times 9\frac{1}{4}$ in. 387 pp. $7.50.—This book deals with the dispersion of finely divided solids in liquid media, and covers the theory and practice of this chemical process, which is essential in the manufacture of rubber, paint, printing ink, pigments, textiles, ceramics, and other industrial products. The book provides a detailed account of the practical uses of wetting agents, the operation of mixing equipment and dispersion machinery, and discusses critically and comprehensively the subject of particle size. The author also discusses several topics previously neglected in the literature of colloids, including dispersion by nonaqueous liquids and dispersion by phase transfer. The chapters are entitled Particle Size, The Solid-Liquid Interface and Wetting, The State of the Dispersed Solid, Rheological Properties of Dispersions, Surface-Active Agents, The Process of Comminution, Mixing, Roll Mills, Ball and Pebble Mills, Disc, Cone, and Colloid Mills, and Dispersion by Phase Transfer (The Flushing Process).

PHYSICAL CHEMISTRY OF HIGH POLYMERIC SYSTEMS. Second Edition. By H. Mark and A. V. Tobolsky. Interscience Publishers, Inc., 250 Fifth Ave., New York 1, N. Y. Cloth, 6 by 9 inches, 517 pages. Price, $6.50.—Reflecting the progress made in most branches of polymer science during the past decade, this new edition has been completely revised and considerably expanded from the first edition (1940). In presenting a condensed but comprehensive selection of basic data on high polymers, the authors have emphasized analysis and discussion of results, with only brief mention of the theoretical foundations and experimental methods. For those interested in obtaining details of the various methods, numerous references have been included. The essentially practical nature of the text is enhanced by the efforts of the authors to present as much data as possible in the form of tables and diagrams and to point out specific cases where methods being discussed were successfully applied.

The scope of the book can be shown by the subjects of the 13 chapters, as follows: geometry of molecules as revealed by diffraction methods; behavior of molecules in electric and magnetic fields; molecular spectra; primary and secondary valence; crystal structure and crystal forces; crystal structure and crystal symmetry; liquids, mesophases, and the amorphous-crystalline character of polymers; thermodynamics of solutions; kinematics of liquids and solutions—viscosity, diffusion, and ultracentrifugation; mechanical behavior of high polymers; step-reaction polymerization; chain-reaction polymerization; and degradation of high polymers. [From the *India Rubber World.*]

NATURAL AND SYNTHETIC HIGH POLYMERS. (2nd Edition.) By Kurt H. Meyer. Published by Interscience Publishers, Inc., 250 Fifth Ave., New

York 1, N. Y. 6½ × 9¼ in. 890 pp. $15.00.—The first edition of this book appeared in 1942 as the fourth volume in the High Polymer Series published by Interscience Publishers, Inc. It complemented the second volume in the series, namely "The Physical Chemistry of High Polymeric Systems" by Mark. Both volumes were actually translations of Meyer and Mark's "Der Aufbau der hochpolymeren organischen Naturstoffe", published some 20 years ago, and "Hochpolymere Chemie," about 10 years ago.

As explained by Meyer in his preface to the current work, the science of high polymers became a science in its own right during the 1930–40 period, and developed at an ever-increasing rate in the 1940–50 period. Accordingly, practically the whole book devoted to the natural and synthetic high polymers had to be rewritten, which accounts for this new edition, although the fundamental concept discussed in the first edition remains unchanged.

As in the first edition, sections are devoted to rubber and gutta-percha and to synthetic or chemical rubbers, with additional references to the rubberlike state appearing throughout the volume. It is interesting to note that the author has dropped quotation marks from the term synthetic as applied to rubber but now uses them around the term chemical as applied to rubber. Most of the data on rubber appears in the chapter on "High Polymeric Hydrocarbons and Their Derivatives."

Considerably larger than the first edition—890 pages, compared to 690 pages—the revised edition is divided into 11 sections, and includes extensive author and subject indexes. [From *The Rubber Age* of New York.]

CHEMICAL INVENTIONS AND CHEMICAL PATENTS. By Edward Thomas. Published jointly by Matthew Bender & Co., Inc., Albany, N. Y., and Clark Boardman Co., Ltd., 11 Park Pl., New York 7, N. Y. Cloth, 6 by 9 inches, 889 pages. Price, $16.50.—Designed to aid patent attorneys, research chemists, and engineers interested in the patenting of chemical inventions, this book presents a complete exposition of the steps involved in preparing a patent. The volume is written around the concept that pitfalls clearly pointed out are likely to be easily avoided, resulting in stronger patents that can withstand future contests. Court decisions are constantly cited as authority for all statements made, and many of the chapters end with a summary of illustrative decisions.

There are 29 chapters in the book, divided into the following six sections: surveying prospective patent rights in an invention; appraising the patent rights formulating the patent rights; construing formulated patent rights; acquiring formal patent rights; and exploiting acquired patent rights. A general appendix of typical patents is included, together with a table of cases and a comprehensive 71-page index. [From the *India Rubber World.*]

SCIENTIFIC AND TECHNICAL ABBREVIATIONS, SIGNS, AND SYMBOLS. Second edition. By O. T. Zimmerman and Irvin Lavine. Published by Industrial Research Service, Masonic Bldg., Dover, N. H. Cloth, 5½ by 8¼ inches, 554 pages. Price, $8.00.—This new edition retains the organization of the preceding book, but includes much new and revised material. In addition to presenting in convenient listings the abbreviations, signs, and symbols used in many scientific and technical fields, the volume stresses the need of greater uniformity in the use of these abbreviations. The value of this work will be evident to all scientists, and the book should contribute greatly to the crusade for standardization.

The text consists of 76 tables of abbreviations, signs, and symbols grouped into 17 sections, as follows: general abbreviations and symbols; Greek alphabet, numerical prefixes, metric abbreviations, mathematics, and statistics; chemistry, chemical engineering, physics, thermodynamics, heat flow, humidity, and radiation; mechanics, hydraulics, acoustics, and illumination; mechanical drawings, materials of construction, and shop terms; electricity, electronics, and magnetics; mapping; railway; aeronautics and aviation; communications; meteorology; military; medicine, botany, and zoology; commerce; astronomy; Latin expressions, states, punctuation, and proofreading; and technical journals. [From the *India Rubber World.*]

STANDARDS ON TEXTILE MATERIALS: 1950. Published by the American Society for Testing Materials, 1916 Race St., Philadelphia 3, Penna. 6 × 9 in. 584 pp. $4.50.—The current edition of this annual compilation includes in the latest form 90 specifications, test methods, and tolerances developed by A.S.T.M. Committee D-13 on Textile Materials. In addition to the standards, there are appendices covering basic properties of textile fibers, a psychometric table for relative humidity, and a yarn number conversion table. Proposed methods of tests and practices for textile products are included, as are extensive sections giving photomicrographs of common textile fibers and of defects in woven fabrics. A convenient table of contents is also included (by subject and A.S.T.M. serial designation) and an index of methods of test. [From *The Rubber Age* of New York.]

CONDENSED CHEMICAL DICTIONARY. (4th Edition.) Published by the Reinhold Publishing Corp., 330 West 42nd St., New York 18, N. Y. 6 × 9 in. 726 pp. $10.00.—Completely revised and enlarged by Professor and Mrs. Arthur Rose of State College, Penna., the latest edition of this internationally known reference book is more complete than ever. It is the latest and most up-to-date dictionary of chemistry, raw materials, trade names and processes, covering all recent developments on chemicals and related materials, and containing some 23,000 separate entries. The new edition, for the first time, includes hundreds of definitions of common chemical terms. As usual, where possible, data are included on standard containers, hazards, and shipping regulations. Many new items have been added in such fields as nuclear chemistry, chemotherapy, and petrochemistry. Many new cross-references have been added to assist the reader in quickly locating desired information. The book is a "must" for all technical libraries. [From *The Rubber Age* of New York.]

CHEMICAL ENGINEERING CATALOG: 1950–51. Published by the Reinhold Publishing Corp., 330 West 42nd St., New York 18, N. Y. 8¼ × 11 in. 1680 pp.—The latest edition of this "bible" of the chemical and process industries, the 35th annual edition to be issued, contains 1654 pages of product facts and technical data supplied by 466 leading manufacturers of processing, general engineering and manufacturing equipment. The traditional system of triple indexes is continued, *i.e.*, alphabetically by company name, by trade name, and by type of equipment. A new functional approach to the classified index has, however, been incorporated for the first time. Now the user of the catalog can look over all headings which appear in the classified index which relate to 14 basic subjects. Among these subjects are heating and cooling, mixing, control, process development, materials and supplies, power, structures and safety.

This new functional approach considerably enhances the growing value of the catalog. [From *The Rubber Age* of New York.]

A GERMAN-ENGLISH DICTIONARY FOR CHEMISTS. By Austin M. Patterson, Professor Emeritus of Chemistry, Antioch College. John Wiley and Sons, Inc., 440 Fourth Avenue, New York 16, N. Y. 1950. xviii + 541 pp. 13.5 × 17.5 cm. Price, $5.00.—For more than thirty years, Patterson's dictionary has been a vademecum for both academic and industrial chemists. The second edition went to press sixteen years ago, and now an expanded third edition has appeared, containing a vocabulary of 59,000 terms. The number of words has thus increased by 40 per cent and most of the additions are drawn from technical fields in which rapid development has been accompanied by a corresponding flood of new *termini technici*, as, for instance, in high-polymer technology, or military chemistry. After an examination of entries concerning fields with which this reviewer can claim a certain familiarity, it appears that the words newly included have been well and wisely chosen.

A part of the purpose of this review is to acquaint chemists with the fact that this valuable library tool has been reëdited; although its widespread use speaks, by itself, for the merits of the work, a brief restatement of its special features at this time may not be amiss. Those possessing a rudimentary knowledge of German will welcome the excellent introduction (reproduced as in the second edition), where common pitfalls in German word and sentence constructions are discussed; the listing of suffixes and prefixes with their various meanings is useful. The vocabulary includes a fair selection of nontechnical words which, nonetheless, are commonly encountered in scientific writing. Particular attention is devoted to terms stemming from arts and crafts, some of them archaic or even obsolete, the meaning of which cannot be guessed at or otherwise deduced. [From the *Journal of the American Chemical Society*.]

LIGHT STIFFENING OF RUBBER *

R. G. NEWTON AND W. C. WAKE

RESEARCH ASSOCIATION OF BRITISH RUBBER MANUFACTURERS, CROYDON, ENGLAND

INTRODUCTION

The form of deterioration which we have designated *light stiffening* can be detected only when the rubber is in the form of a thin film, as it is, for example, in light-weight single-texture proofings. The implications of this work, however, extend far wider than its immediate application to thin proofings, important though this is, and we have no reason to suppose that the surface crazing seen on articles of rubber exposed to sunlight is not essentially the same thing. It is convenient, for reasons which appear later, to distinguish these two forms of deterioration of rubber, even though chemically and energetically they may have the same fundamental basis.

Light stiffening is the noticeable increase in the bending modulus of thin sheets of rubber which occurs with exposure to light and air. This increase is easily observed by handling proofed fabrics so exposed, and in normal speech we refer to a "stiffening" of the article. It is an effect greater at the surface and decreasing with penetration into the bulk rubber, and for this reason is subjectively evident only where the "surface layers" form an appreciable proportion of the total thickness of the rubber. This deterioration becomes essentially a defect confined to thin proofings and other articles, the rubber parts of which form a sheet or layer a few thousandths of an inch in thickness.

Continued exposure of rubber, long after light stiffening has become evident, gives rise to a resinous film on the surface. In the case of a thicker piece of rubber, the stiffening is not apparent, and the earliest sign of deterioration in light and air is the formation of this resinous skin. The formation of the skin on very thin proofings or films of rubber causes a curling or twisting of the film or proofing in the sense that would be anticipated if the formation of the skin were accompanied by a contraction, *i.e.*, the proofing or film curls with the surface on which the resinous film has formed innermost. With thick rubber the forces which would be required to cause the rubber to curl are greater than the strength of the resinous film. This we assume is the cause of the formation of fine cracks all over the surface of the skin, since there is no preferred orientation for these cracks and they never penetrate the rubber, but are always confined to the surface layer of resinous material. This phenomenon is usually called *surface crazing*, and we see no need to change its appellation. It represents, in all probability, a later stage in the deterioration which we have called light stiffening, and is, we believe, differentiated from it only phenomenologically and not causatively. Light stiffening is confined to thin rubber, articles of which are usually rendered useless by reason of their stiffening, and also by the consequent fracture of the stiffened rubber long before any resinous skin is evident. Surface crazing cannot occur until resinification has progressed to a finite and measurable depth from the surface, and then only if the article is

* Reprinted, with a few omissions, from the *Journal of Rubber Research*, Vol. 19, No. 2, pages 9–16, February 1950, and No. 3, pages 17–27, March 1950.

sufficiently rigid to resist curling forces. It is easily distinguishable from the familiar weather cracking now universally accepted as due to atmospheric ozone.

Most of the new experimental work reported in this paper refers to the light stiffening of thin proofings, but, for some of the work, films of rubber 20 to 80 microns thick were used. With the former a very simple technique was evolved and is discussed in some detail, as it may form a useful means of factory control and evaluation to replace the subjective and unsatisfactory tests at present applied. No method of artificially accelerating the deterioration seems feasible at present, though extensive trials have been made with various mercury vapor lamps. Importance therefore attaches to the work here reported on seasonal variations and the behavior of standard proofings.

EXPERIMENTAL PROCEDURE

SIMPLE RAPID METHOD

In this method of measuring light stiffening, suitable strips of proofed fabric were exposed to sunlight, and the stiffness was assessed before and after exposure by determining the bending modulus. The great advantage of this procedure was that its extreme simplicity enabled many hundreds of measurements to be made without great effort. The details were as follows: Strips of the proofed fabric measuring 1.3 cm. wide (0.5 inch) and at least 6 cm. long were cut from the sheet with scissors, and a hole 4 mm. in diameter was punched in the middle of the width, 5 cm. from one end. The part of the strip remote from the 5 cm. length was not used for testing, and was available for recording sample numbers, date of exposure, and the like, and for pinning the sample to a support. In measuring the stiffness, the hole was placed over a similar hole in a metal support 2 cm. long and at least 1.3 cm. wide, a similar piece of metal being clamped on the top, with a locating pin passing through all three holes. Part of the test strip 2.0 cm. long and 1.3 cm. wide was thus firmly clamped, the 4 cm. end of the test-length thus becoming a cantilever and sagging under its own weight. This is illustrated by the photograph of the apparatus and test-pieces given as Figure 1. The deflection of the end of the cantilever, below the horizontal, was measured in cm., and the effective bending modulus of the composite proofing calculated from the expression:

$$E = (12050W + 4510w)/T^3y$$

where E = bending modulus in kg. per sq. cm.; W = applied weight in gram (see below); w = weight of test length (4.0 × 1.3 cm.) in gram; T = thickness of proofed fabric in hundredths of an inch; and y deflection of end in cm. The heterogeneous collection of symbols and numbers was employed for convenience, the thickness being measured on the ordinary thickness gauge (reading in 0.001 inch), while the whole calculation was performed graphically. As the sample stiffened the deflections became smaller until it was necessary to add more weights to produce measurable deflections; this was done by hooking bent pieces of wire, of known weight, into the end of the sample.

The moduli determined by this method are in no sense absolute, but it is claimed that they are adequate for the purpose. Since the increase observed is frequently a few thousand per cent, it is obvious that accurate measurement is not called for, provided sufficient discrimination can be shown to exist. The coefficient of variation of a single measurement of bending modulus was found to be 10 per cent, while the coefficient of variation for the combined errors of

measurement, variability of samples, and of the differential response of samples to environment was found to be 90 per cent. Set against the very large increases of bending modulus, this was held to be satisfactory, as is illustrated by examples later in this paper.

Since these measurements are in no sense absolute, it is necessary to employ a control sample exposed under the same conditions as the sample or samples under test. It is convenient always to employ as this control the same standard proofing. This implies that the standard material does not change in stiffness if it is kept in darkness, control samples being cut from it for exposure as necessary.

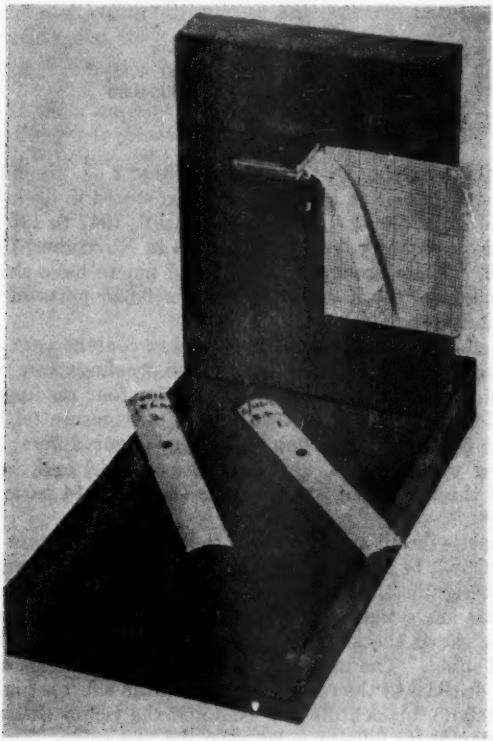


FIG. 1.

Results accumulated over a period of 3 years show that the changes which do occur during storage in the dark for this period are not important when compared with the magnitude and rate of the changes induced by light. Table 1 shows that the initial stiffness appears to double in about 3 years; *i.e.*, an increase of 100 per cent, compared with at least 850 per cent which occurs with 20 days' exposure.

Table 1 shows also the actual stiffness after the 20 days' exposure; the figures are naturally very variable because the amount of sunshine was not the same in each period, but there is no evidence to show that the stiffness after exposure has undergone any systematic change during these 2 years.

TABLE 1

BEHAVIOR OF THE STANDARD (GR-S) SAMPLE

Date	Stiffness of the unexposed sample (kg./sq. cm.)	Stiffness after exposure to sunlight for 20 days (kg./sq. cm.)	Percentage increase in stiffness
March, 1945	260, 255	2500, 2500	870, 880
December, 1945	280	*	*
May, 1946	340, 380	*	*
May, 1946	340, 365	6300, 4400	1740, 1100
June, 1946	230	3750	1500
November, 1946	365, 380	*	*
November, 1946	430, 450	*	*
January, 1947	415, 495	*	*
April, 1947	360, 360	4000, 4700	1020, 1200
April, 1947	395, 450	4000, 4000	920

* Not used in outdoor tests.

Figures are also available for two natural rubber 2 oz. proofings, *i.e.*, proofings affording a very sensitive test for stiffening, stored in darkness. A white proofing changed from 226 kg. per sq. cm. in April, 1947 to 190 in November, 1949, and a yellow proofing gave a figure of 314 in November, 1946 and 320 in November, 1949. These proofings may be said not to have changed through the period considered. Both proofings contain 0.625 parts of a proprietary nonstaining antioxidant.

The general effects of thickness, color, and wax content were investigated in a planned experiment, in which 36 types of GR-S proofings were used. Table 2 gives figures for the mean increase in stiffness for four readings obtained by measuring duplicate samples after two periods of exposure (either 46 and 60 days, or 44 and 58 days). The samples include four different colors, three different proofing weights (2, 4, and 6 oz. per sq. yd.) and, hence, different thicknesses, and three different wax contents (2, 7, and 14 parts per 100 parts of rubber).

The mean results for all proofings with the same wax content were: 2 parts, 985%; 7 parts, 890%; 14 parts, 975%; and it is evident that changes in the wax content have no significant effect on the stiffening. It is also evident that proofing thickness has a significant effect because, in every case but two, the thickest proofing shows the least stiffening, while the thinnest proofing shows the greatest stiffening. The influence of proofing color is not so self-evident, but a statistical analysis of the results shows that the effect is highly significant (P = less than 0.001), black stiffening least and the yellow compound of Type II most. The significant difference between the two yellow compounds is due to the inclusion of 10 parts of brown substitute in the Type II compound and not to any difference in the shade of the color, which seemed a perfect match.

TABLE 2

PERCENTAGE INCREASE IN STIFFNESS OF GR-S PROOFINGS

Color of proofing	Yellow, Type I			Yellow, Type II			Green			Black			
Wax content	2	7	14	2	7	14	2	7	14	2	7	14	Mean
Proofing weight													
2 oz. per sq. yd.	1600	1360	1460	3680	2550	2250	1340	1000	1700	460	750	950	1590
4 oz. per sq. yd.	1100	1000	350	1430	1180	870	820	750	880	120	510	970	830
6 oz. per sq. yd.	410	410	210	330	320	790	430	520	1000	86	290	280	420
Mean		880			1490			940			490		950

This leads naturally to a consideration of the effect of other differences in compounding.

We consider firstly differences in the rubber used. For Neoprene proofings, the mean percentage increase in stiffness produced by the different variables (mean of 72 results, half of which represent 31, and half 45 days exposure) are given in Table 3.

None of these effects is statistically significant at the 5 per cent level, but that for the different colors is nearly significant and might well be regarded as such; thus in this case also, the black proofings stiffen least, but the difference is not nearly so marked as in those prepared from GR-S. Neither the proofing thickness nor the wax content appears to have any effect on stiffening, although there is a suggestion that those with least wax show the smallest stiffening.

Butyl compounds softened on exposure to light, irrespective of thickness, color, or wax content. The softening was slight (about 20 per cent decrease in stiffness after 75 days' exposure), but definite and persistent. It is thus seen that the type of polymer present is not without significance, although stiffening does not run directly parallel to what is regarded as their resistance to aging, as measured by alteration of physical properties after aging in the Geer oven. Both Butyl rubber and Neoprene are much less reactive towards oxygen than

TABLE 3

PERCENTAGE INCREASE IN STIFFNESS OF NEOPRENE PROOFINGS

Color	Wax content	Proofing thickness
Green, 1000	2 parts, 730	2 oz. per sq. yd., 870
Yellow, 935	7 parts, 910	4 oz. per sq. yd., 710
Black, 635	14 parts, 950	6 oz. per sq. yd., 990

is natural rubber or GR-S and, as is apparent later, this is the deciding factor in determining the light stiffening reaction.

RESULTS OBTAINED WITH LIGHT-WEIGHT PROOFINGS

A definition of light stiffening was given in the introduction, and it might be useful here to review the validity of the definition before describing the effect of variation in material and conditions of exposure. Proofing exposed to air and light shows stiffening only if the rubber face is toward the light. Of two identical proofings, one exposed in daylight and one at night, only that exposed to light stiffened. This observation excludes ozone attack as a causative factor since the atmospheric ozone concentration is the same by night as by day. The heating effect caused by exposure to bright sunlight is not alone sufficient to account for the effect, since a coating of black tire paint prevented continued stiffening. Samples placed in stoppered glass test-tubes stiffen normally, but the stiffening is inhibited by wrapping the tube in black paper. Since the penetrability of the rubber by light will be limited, it is obvious that only surface layers will be affected and, hence, that thick proofings will stiffen less than thin proofings. Color will influence this penetrability, but it will also alter the heat absorption characteristics of the material.

INFLUENCE OF THE WAVE LENGTH OF LIGHT

Experiments on the influence of the wave length of the incident light were carried out mainly on GR-S proofings. In view of the nature of the results ob-

tained, it will become obvious that they are, in general, applicable to natural rubber.

The observation early in the work that the stiffening occurred quite normally when the sample was exposed in a stoppered glass tube showed that the short ultraviolet radiation is not essential for the process, since the transmission of ordinary glass is small below 3000 Å. It also enabled simplification of the experimental technique, since glass jacketing can be used to protect gelatin filters without much loss of efficiency.

It was decided to use a direct method of studying the effect, by exposing a proofed fabric to light of different wave lengths and determining the amount of stiffening. The simplest method would have been to isolate the different wave lengths by filters of the appropriate colors, but the fraction of the incident light which is transmitted by such filters is small (usually less than 2 per cent), and, hence, the experiment would need to be of very long duration if the sample were to be supplied with equal energies of incident light. Thus, if a sample required

TABLE 4

WRATTEN FILTERS USED IN ISOLATING EFFECT OF WAVE LENGTH OF LIGHT

Filter used	Approximate wave length below which there is substantially no transmission	Percentage of energy available in sunlight (for wave lengths shorter than 540 mμ) transmitted by the filter*
1	360	80
2	380	68
2A	410	64
3	440	45
5	470	26
12	500	13
16	520	4
21	540	0
22	555	0
23	570	0

* In comparison, glass transmits 83 per cent.

20 days to show a certain degree of stiffening when exposed to direct sunlight, it would need 5½ years behind a filter with a transmission factor of 1 per cent before it had received the same amount of energy and, naturally, the two experiments would not be comparable. To avoid this difficulty, a different approach was used; other types of filter are available which transmit freely all radiation of wave lengths greater than a certain value, and, hence, have much higher transmission factors. The series of Wratten filters shown in Table 4 were used, and it can be seen that they cut off at increasing wave lengths, while even filter 23 transmits 25 per cent of the incident visible radiation.

These filters were in the form of gelatin squares (3 × 3 in.) which were rolled up inside boiling tubes so that samples of proofing could be exposed to sunlight in a simple manner which prevented moisture from attacking the gelatin and also removed the sample from effects of humidity and ozone. As controls, proofing samples were also exposed in a plain glass tube and directly to the atmosphere.

The proofing used contained some wax and 4 parts of yellow coloring ingredient and was, as already mentioned, based on GR-S.

Up to 67 days' exposure, the results were as shown in Figures 2 and 3, from which it can be seen that all the filters produce marked reduction in stiffness

compared with plain glass and that filters 21, 22, and 23 do not permit any light stiffening. (Actually these three filters allow a slight and equal amount of stiffening which may be due to some other cause. As the effect is equal with all three, it has been ignored except in so far as it has been used to form a new base-line from which to calculate the stiffening produced by the other filters.)

It is also noticeable that the sample in the plain glass tube has stiffened much more than the one exposed directly to the atmosphere. This may be due either to a leaching of oxidation products from the sample by rain, or tendering of the fabric backing, or to differences in heating effects. As will be indicated later, this last is the most probable explanation, and there will be a greater difference in heating effect between all the exposures behind gelatin filters on one hand and that with glass alone on the other than between the various filters which may be regarded as comparable from the point of view of heating effects.

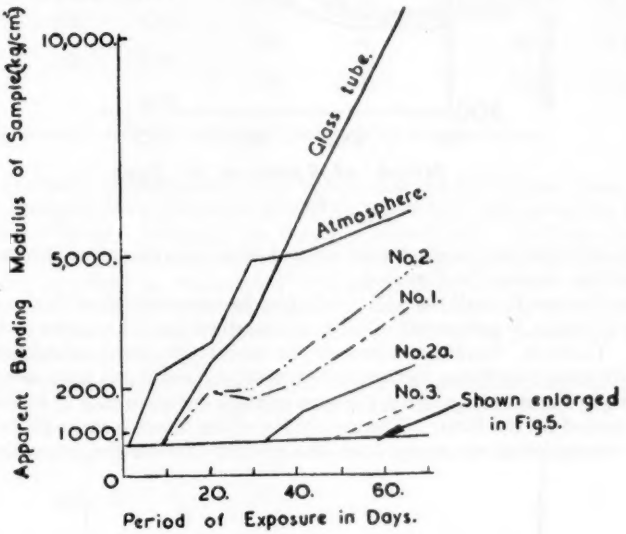


FIG. 2.

The relative effects produced by filters 1 and 2 are in the reverse order from that expected from their transmission characteristics; both of these filters are, however, known to be unstable and, as will be shown below, there is reason to believe that one (or both) has altered.

It is evident from Figures 2 and 3 that any stiffening produced by filters 21–23, or even by filter 16, is negligible, and hence wave lengths longer than about 540 mμ have only an insignificant effect. It is possible to calculate the amount of energy below 540 mμ which is transmitted by each of the filters, by using the published transmission curves. In addition, by using a chart of the spectral distribution of solar radiant energy such as that given, by Crabtree and Kemp[1], the percentage of such energy as available in sunlight can be tabulated. The figures of these authors for the atmospheric conditions which they refer to as "Air-mass 1" have been used in Table 4, and the amount of stiffening after

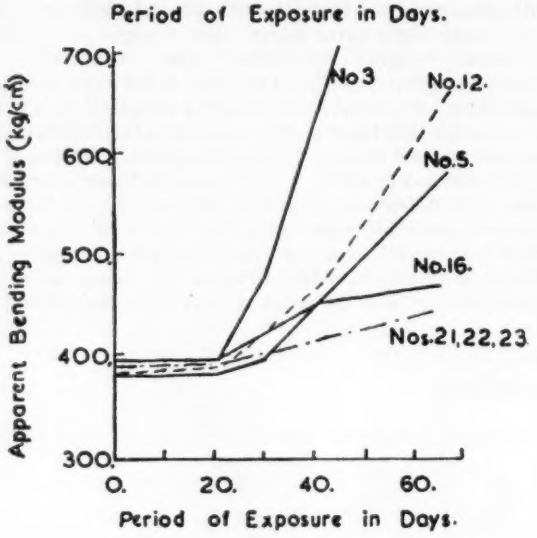


FIG. 3.

67 days' exposure has been plotted against these energy values (known as percentage filter factors) in Figure 4.

It can be seen that all the points fall close to a smooth line with the exception of filter 2, which, together with No. 1, is described by the makers as being unstable. There is, therefore, some doubt about the total calculated energy passed by these two filters, but for the present purpose it has been assumed that the curve in Figure 4 represents the true relation between rate of stiffening and energy passed by the filter. The instability of the filters is more likely to allow greater transmission of energy than the reverse (due to decomposition of the

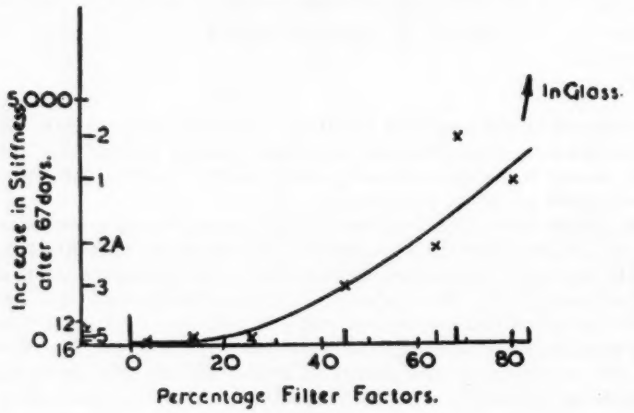


FIG. 4.

TABLE 5

CALCULATION OF THE RELATIVE ACTIVITY OF DIFFERENT WAVE LENGTHS IN PRODUCING STIFFENING

Filter used	"Calculated" stiffening after 67 days' exposure (kg. per sq. cm.)	Filter factor (540)	Change in stiffness	Change in energy	Relative activity of the energy (4)/[(5)×10³]	Wave length of energy involved* in mμ	Equivalent energy in kcal. per g.-mol.
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
1	3,550	0.80					
			1,300	0.16	75	385	74
2A	2,250	0.64					
			1,300	0.19	81	440	64
3	950	0.45					
			650	0.19	34	475	60
5	300	0.26					
			200	0.13	15	505	56.4
12	100	0.13					
			80	0.09	9	525	54.2
16	20	0.04					
			20	0.40	5	540	52.7
21	0	0.00					

* Based on differences between the steeply-rising portions of the transmission curve.

sensitive dyestuff); consequently filter 2 has changed more than filter 1. If both have changed, then the curve should lie below the point given by filter 1 but, in view of its general trend, this does not seem likely. In Table 5 all the experimental points have been corrected to bring them on the curve, the new values being described as "calculated" stiffening after 67 days. In the subsequent columns of Table 5 the differences in rate of stiffening are divided by the differences in filter factor to give the relative activity of the different wave lengths in producing stiffening.

In Figure 5 the relative activity of the energy in producing stiffening (Column 6 of Table 5) is plotted against the mean wave length of the energy

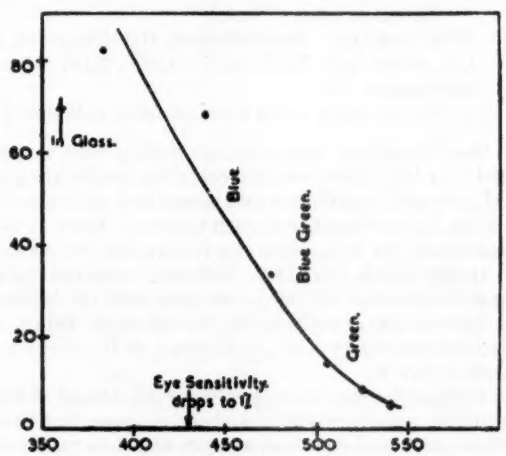


FIG. 5.

(Column 7), and it can be seen that very little stiffening is produced by green or even blue light, but that the invisible ultraviolet radiation increases in activity as the wave length decreases. Column (8) gives the energy equivalence of the wave lengths given in Column (7) calculated according to the Einstein law of photochemical equivalent, and it is seen that the stiffening action moves in the same sense as the energy content of the incident light, though not proportional to it.

SEASONAL VARIATION IN STIFFENING

The work on light stiffening was initiated in 1944, when the industry was especially concerned with the weathering of very thin GR-S proofings. Thus all the initial work was carried out on proofings which are of a type no longer made in the United Kingdom, and the standard material, being based on GR-S and having a coating of only 2 oz. per sq. yd., may well not be suitable for use as a control for present-day qualities. It is thus clearly of importance to use natural-rubber proofings of more normal weights, but it is also clear that 4-oz. proofings stiffen at about half the rate for 2-oz. materials, while 6-oz. proofings stiffen at only one-quarter of the rate, and hence the experiments would be much more lengthy.

Accordingly, an approach was made to two Member Firms of the R.A.B.-R.M. (A and B), who had shown particular interest in this work, with the request that they would prepared a 2-oz. and a 4-oz. high-rubber-content proofing for the purpose of examining the seasonal variation in stiffening.

The proofings supplied and used in this extended trial were as follows:

1. Standard GR-S proofing of 2-oz. weight.
2. Another light weight (2 oz.) GR-S proofing.
3. Firm A. *Drab proofing.* Smoked sheet, 100; zinc oxide, 5; whiting, 15; MBTS, 1.25; TMT, 0.156; sulfur, 2.3; stearic acid, 1.25; antioxidant, 0.625.
4. Firm A. *Yellow proofing.* As drab, but with the addition of color, 0.625.
5. Firm A. *Blue proofing.* As yellow.
   (Proofings 3, 4, and 5 were also 2-oz. proofings, and were vulcanized by dry heat.)
6. Firm B. *White proofing.* Smoked sheet, 100; lithopone, 24; zinc oxide, 4.3; sulfur, 3.0; MBT, 0.67; TMT, 0.167; stearic acid, 0.67; antioxidant, 0.5.
   (The proofing was a 4-oz. proofing vulcanized by dry heat.)

Samples of these proofings were exposed during each month of the year from August, 1947, to July, 1948. and the complete results are given in Table 6.

August, 1947, was particularly hot and sunny and, at the end of the month, some of the samples had stiffened too much to permit them to be tested, much curling having occurred; for this reason the 15-day and 25-day figures are given in place of the 31-day value. Very little stiffening occurred during December, and the samples were therefore left out in the open until the beginning of March, and this 91-day figure is also given between the values for February and March; in most cases it is substantially equal to the sum of the three monthly figures given immediately above it.

From Table 6, it can be seen that there is no significant difference between the two GR-S samples, or between them and the blue one, but the yellow sample apparently stiffens more and the drab sample seems to stiffen less; the thick white sample is, however, much more resistant to stiffening than the others.

TABLE 6

RESULTS OF MONTHLY EXPOSURE TESTS

Month	Standard GR-S	Other GR-S sample	Natural rubber: Firm A: Drab	Natural rubber: Firm A: Yellow	Natural rubber: Firm A: Blue	Natural rubber: Firm B: Thick white
August—15 days	1090	1300	970	3000	2060	730
25 days	—	6700	—	13500	4200	2030
September	2200	2500	2000	2000	2000	540
October	1300	1300	1050	2200	1900	250
November	500	250	500	400	350	100
December	50	0	100	250	100	0
January	50	40	50	20	10	0
February	450	650	900	800	700	450
91-days	600	900	1000	1100	750	450
March	1650	1500	1300	2000	1550	450
April	2300	2300	1750	2500	2500	1000
May	2300	3000	2500	2700	1800	1100
June	2600	2500	2000	2300	2000	1300
July	2200	1800	1200	2400	1750	1500

Note.—The figures in the table are percentage increase in stiffness.

Although there are probably real differences in stiffening between the five thin samples, *e.g.*, the yellow sample apparently stiffens more than the drab, they all stiffen so much more than the thick one that it is convenient to consider them all together when discussing the correlation with sunlight. Thus the mean percentage increase in stiffness for all five thin samples (three only for August, the 25-day values being used) is given in Table 10, together with the values for the thick sample. The degree of accuracy of measurement was reëxamined and was found to be as small as before, but an annual change was found in the stiffness of the unexposed samples; they were 10 per cent stiffer in December than in July, and it is assumed that this was due to an effect of temperature.

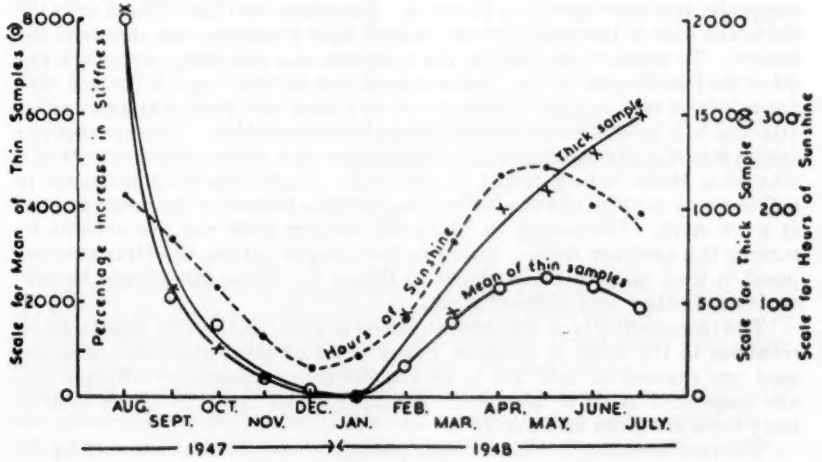


FIG. 6.

The number of hours of sunshine per month was obtained from the Meteorological Office at Croydon Airport, through the kind assistance of the Air Ministry. The Airport is about 2 miles from the R.A.B.R.M. Laboratories and the sunshine figures are therefore appropriate for the Laboratories.

The results for the thick sample, the mean of the thin samples, and the number of hours of sunshine, are given in the graph, Figure 6, whence it can be seen that the general progress of stiffening is essentially similar for all the proofings, and that there is a qualitative agreement between these curves, and that for the number of hours of sunshine, except that the sunshine is relatively more efficient in the summer and less efficient in the winter.

The relative amounts of stiffening in different months of the year are very different, a 20-fold to 100-fold difference being possible between winter and summer. This variation is largely explained by the changes in the total amount of light received by the samples, but the variation in stiffening is greater than the variation in amount of light, and this may be due to the effect of heating of the samples in summer. There is evidence[2] to show that light can profoundly modify subsequent heat aging in darkness and it is thus likely that a combination of light and heat would produce considerably more stiffening than either separately. Tobolsky and Mesrobian state that the absorption of oxygen by GR-S is greater in the presence of light and that this increased rate of absorption due to light is greater at higher temperatures[3].

EXPERIMENTS WITH THIN FILMS OF NATURAL RUBBER

An alternative procedure using thin films cut with a microtome from thicker rubber was introduced at a late stage in this investigation. Rubber, in the form of pieces about 1 × 3 cm. and 0.1 inch thick was cemented to the freezing stage of a heavy sledge type microtome[4] frozen with liquid carbon dioxide (obtained by using a cylinder of the gas in an inverted position) and films approximately the size of the rubber piece cut with thicknesses varying from 20 to 80 microns. Two small pieces of pure-gum rubber were cemented with a self-vulcanizing natural rubber cement on to each end of the thin film, forming a composite test-piece shown in Figure 6. Aluminum was then folded over the thickened ends of the test-piece and pressed tight to squeeze and thus hold the rubber. To measure the stiffness, the cross wire of a travelling microscope was set at the lines formed by the thicker end rubbers and the length measured both unloaded and with various weights placed on a small pan, itself of known weight, attached to a hook, fastened to the folded aluminum holder. The modulus was calculated from the mean of two or three stress and strain measurements, the maximum strain not exceeding 10 per cent. These thin films increased in stiffness very rapidly, and the further stage of resin formation becomes apparent in a few days. The curling to which this usually gives rise was avoided by turning the specimen daily. Owing to their fragile nature, the films were exposed in hard glass tubes, as shown in Figure 7. These tubes could be conveniently flushed with different gases.

The reproducibility of the measurements is good, and can be illustrated by reference to the series of constant values obtained when the first compound used was exposed to light but in an atmosphere of oxygen-free nitrogen and also suspended in air in darkness. The appropriate modulus figures in arbitrary units are given in Table 7.

The results obtained with a simple pure-gum compound accelerated by diphenylguanidine are shown in Figure 8; replication of part of the experiment

being shown on the same diagram. The films used in this experiment were approximately 40 microns thick and were examined during and after exposure by an infrared absorption spectrometer. The spectra show, in addition to the normal absorption bands for rubber, the increasing occurrence of the —C—O— linkage which, as is discussed below, is probably to be associated with the peroxide link.

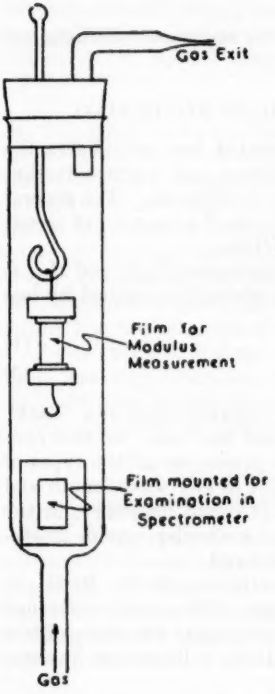


FIG. 7.

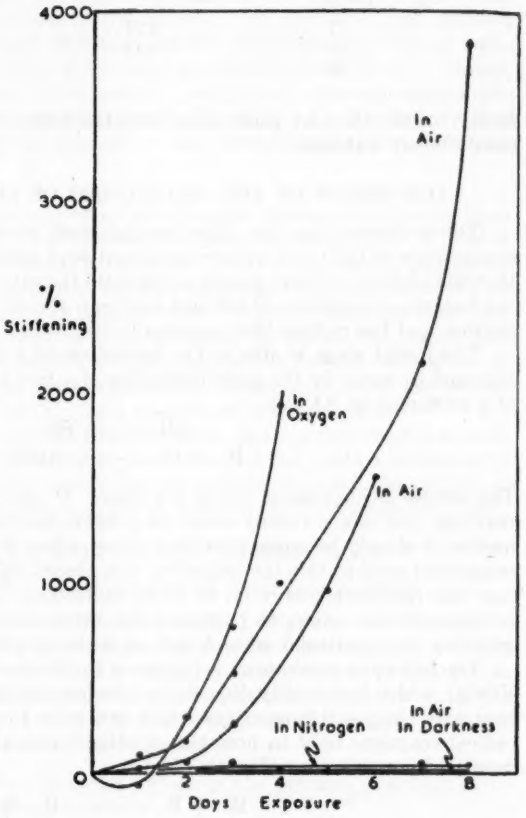


FIG. 8.

Carbonyl and hydroxyl absorption bands were also present, and they increased in intensity during the period of exposure of the sample. By the end of 7 days' exposure, absorption due to the double bond had completely disappeared, showing that the rubber had become fully saturated.

It is obvious that thin films cut with a microtome and used for modulus and absorptiometric measurements can form a valuable tool in the investigation of this type of rubber deterioration, although they suffer from the disadvantage that they cannot be exposed to the full severity of the elements, as they are too

TABLE 7

Period of exposure (days)	Modulus (light but no oxygen)	Modulus (oxygen but no light)
0	0.495	0.765
1	0.52	0.80
2	0.495	0.82
3	0.77	—
4	0.59	—
5	—	0.745
7	0.77	0.745
8	0.75	—
35	—	1.09

flimsy. Protection by glass seems essential unless the exposure conditions are continuously watched.

DISCUSSION OF THE MECHANISM OF LIGHT STIFFENING

The evidence from the experimental work presented here establishes the concurrence of light and oxygen as the cause of stiffening, and suggests further that the addition of heat greatly accelerates the rate of stiffening. The general mechanism of oxidation of rubbers has been the subject of a number of recent studies, and the picture that emerges is briefly as follows.

The initial stage is always the formation of a hydroperoxide[5], and this is assumed to occur by the prior formation of a free hydrocarbon radical by loss of a proton as in (1), (2):

$$RH \longrightarrow R\cdot \qquad (1)$$

$$R\cdot + O_2 \longrightarrow ROO\cdot \qquad (2)$$

The precise mechanism of this is not clear. It can probably occur as a "dark" reaction, and can certainly occur as a light-catalyzed reaction. In this connection it should be noted that zinc oxide, which is present in all the types of compound used in this investigation, can absorb light of any wave length and pass the resultant energy on to other molecules. It is not necessary, in the presence of zinc oxide, to postulate the presence of molecular species photosensitive to a particular wave length or wave length band.

The initiation mechanism is by one of the three active species R·, ROO·, or ROOH, which last readily dissociates into free radicals. We are not concerned here with the possible reactions which can serve to propagate the chain of free radical reactions only to note the possible terminations. These can be summarized by expressions (3), (4), (5):

$$R\cdot + R\cdot \longrightarrow R{-}R \qquad (3)$$

$$R\cdot + ROO\cdot \longrightarrow ROOR \qquad (4)$$

$$ROO\cdot + ROO\cdot \longrightarrow ROOR + O_2 \qquad (5)$$

In addition to these there could be, and undoubtedly are, intermediate forms of the free radical R· in which the position of the active odd electron along the polymer chain gives rise to an internal instability followed by molecular scission, one of the fragments perpetuating the chain reaction, the other being a "dead" or "cold" molecule. Decomposition of the hydrocarbon radical in this way obviously leads to a reduction in molecular weight.

The termination reactions shown in Equations (3) to (5) all lead to the formation of larger molecules, and are of the type called cross-linking reactions.

Cross-linking, when inter- and not intramolecular, leads to higher molecular weight and increased modulus of the molecular aggregate.

In the absence of oxygen, it might be expected that formation of hydrocarbon radicals as in (1) could lead to a chain reaction terminating by reaction (3). This does not happen, as no stiffening can be detected in the absence of oxygen. Oxygen is an essential part of the radical reaction chain, though at oxygen pressures sufficient to establish this reaction chain, but relatively low, termination (3) would become of more importance. At normal oxygen pressures termination is predominantly by reactions (4) and (5)[3]. The infrared absorption spectra is consistent with the view that reaction (4) or (5), or both, are the final step as the intensity of the band attributed to the R—O— linkage increases steadily throughout the exposure. Insufficient reference compounds are available to distinguish between R—O—R and R—O—O—R and R—CH—CH—R, but the observed absorption band frequency is lower than usu-
\ /
O
ally found with ordinary ethers, an effect which might be expected in going from R—O—R to R—O—O—R. The epoxide frequency is not known. The wide absorption band due to the overall absorption of the double bond disappears during the course of the exposure, and the final product is fully saturated. This loss of unsaturation could arise in several ways. Among them we may consider: (1) through the formation of intramolecular peroxides, *i.e.*, cyclic peroxides; by secondary decomposition of the peroxide free radical leading to (2) the formation of epoxides; or by the secondary decomposition of the hydrocarbon free radical, leading to (3) chain scission at the double bond.

Recent work of Bolland[6] establishes the first as an important reaction leading to loss of unsaturation, and it seems probable that the chain mechanism in oxidation involves four steps in place of the two usually assumed, the additional steps being caused by the formation of a cyclic peroxide in the manner indicated.

DISCUSSION OF TECHNOLOGICAL SIGNIFICANCE

EASE OF ASSESSMENT AND COMPARISON WITH OTHER TESTS

One of the concrete results which have emerged from this investigation is the utility of the simple cantilever modulus test described in this paper, and it is interesting to compare the behavior of proofing as measured by this test and as assessed subjectively by the industry. It is understood that workers in the proofing industry assess the amount of weathering which has occurred after exposure by means of one or all of the following:

(1) A thumb-nail test, in which the surface of the proofing is scratched or plucked with the thumb-nail.

(2) A simple-fold test, in which the proofing is folded sharply with the rubber surface outwards.

(3) An envelope-fold test in which test (2) is followed by a second fold at right angles to the first, thus producing a square corner.

Samples of the standard material were exposed out-of-doors for periods up to 26 days; the stiffness was then measured and the three simple tests carried out. The stiffness of the samples increased by amounts up to about 1600 per cent, but in no case did either of the folding tests (2 and 3) reveal any deterioration of the surface when the folds were straightened out. The scratching test (1) was also disappointing. For the first two days' exposure (up to 80 per cent

increase in stiffness), it was not possible to damage the surface by scratching with the thumb-nail, and the worst that could be done was to produce a dull mark. After 5 days (450 per cent increase in stiffness) repeated scratching would remove a little rubber from the surface, but it required 7 days' exposure (650 per cent increase in stiffness) before a single very firm scratch would remove any rubber. Even after the longest period given (26 days and 1600 per cent increase in stiffness), it was difficult to remove more than just the surface layer.

It thus appears that the modulus test is a much more sensitive method of following changes resulting from outdoor exposure than any of the other simple tests, and it is obvious that it would therefore be of much greater value in discriminating between proofings and thus assessing their behavior and possible life. No artificial aging test can replace out-of-doors exposure, and it is suggested that this modulus test is suitable for normal industrial use, providing a control is also exposed. It becomes obvious from this work that the best accelerated aging test for use by manufacturers is the preparation of small quantities of very light-weight proofing, say 2 oz. on very light material, *e.g.*, parachute Nylon from the compound they wish to test. This should be exposed to bright sunlight in spring or summer, when a week's exposure will produce substantial stiffening, *i.e.*, it is possible to submit the proofing compound to an accelerated aging test, though not the actual proofing as required. However, since it is the compound that deteriorates and not the particular rubber-textile combination employed, this does not constitute a disadvantage except in so far as an additional laboratory-scale spreading is required.

GENERAL DISCUSSION OF DETERIORATION

The general picture of light stiffening set out in this paper indicates that the only efficient way to prevent the deterioration is by means of substances which interfere with the propagation of the reaction chain. Such substances are antioxidants and deactivators alone[7]. It has recently[8] been reported that there is some advantage to be gained by the use of mixtures of antioxidant and deactivator. Compounding cannot be expected to have much influence on stiffening, indeed, Mesrobian and Tobolsky[3] report that clay has an accelerating effect on photoactivated oxidation. Waxes, it has been shown here and elsewhere[3] are without effect.

A method of protection second to interference with the oxidation reaction is protection against light. It is not necessary for the light to be direct sunlight for it to have a deleterious effect. Casual exposure indoors to ordinary daylight has been shown sufficient to catalyze the initial formation of peroxide[2], and this has recently been emphasized by a worker in the same laboratory[5], who has shown that oxidation under light from a relatively weak source increases from zero through a maximum to a constant value. The service life of proofings can be greatly increased if they are protected from ultraviolet light, and surface stiffening would be almost completely prevented if the proofings were used only in light from the long wave length end of the spectrum; namely, green, yellow, or red light.

To this end, packaging in suitably dyed wrappers would enable the article to be seen without danger of deterioration when placed in shop windows and the like. Where possible, dark colors or even black loading enables the light catalyzed oxidation to be confined to a lesser depth of the rubber and hence minimize stiffening. Some improvement might also be expected from the in-

corporation of ultraviolet adsorbents in the compound. These materials, frequently esters, blooming to the surface of the rubber, may absorb sufficient energy to ameliorate the position through the presence of such a surface bloom may of itself be a disadvantage. It is hoped to investigate these possibilities in the near future.

ACKNOWLEDGMENTS

The authors' thanks are due to (Miss) R. Elliott for the exposure tests and the measurements, to J. Mann for taking the infrared absorption spectra of the thin films exposed, and interpreting the results, and to the staff of the Meteorological Office of Croydon Airport for supplying figures for the hours of sunshine. Acknowledgment is also made due to the Controller of Chemical Research, Advisory Service on Plastics and Rubber, Ministry of Supply, MX4b, under whose auspices the work on GR-S was carried out, for permission to include work reported to him.

REFERENCES

[1] Crabtree and Kemp, *Ind. Eng. Chem.* **38**, 278 (1946).
[2] Morgan and Naunton, *Proc. Rubber Technol. Conf.* 1938, p. 599.
[3] Mesrobian and Tobolsky, *J. Polymer Sci.* **2**, 463 (1947).
[4] Precision Plate Type, made by M. S. E., Ltd.
[5] Morgan and Naunton, *Proc. Rubber Technol. Conf.* 1938, p. 599; Farmer and Sundralingam, *J. Chem. Soc.* 1943, p. 541; Bolland, *Quart. Revs. Chem. Soc.* **3**, 1 (1949).
[6] Bolland and ten Have, *Trans. Faraday Soc.* **45**, 93 (1949).
[7] Stafford, *Proc. 2nd Rubber Technol. Conf. London*, 1948, p. 94; Le Bras and Salvetti, *Proc. 2nd Rubber Technol. Conf. London*, 1948, p. 123.
[8] Stafford, *Proc. 2nd Rubber Technol. Conf. London*, 1948, p. 94.

THE OXIDATION OF RUBBER VULCANIZATES*

HOLGER LETH PEDERSEN

CHEMICAL RESEARCH LABORATORY, A/S NORDISKE KABEL- OG TRAADFABRIKER, COPENHAGEN, DENMARK

The slow, spontaneous deterioration in the tensile strength and elongation of rubber vulcanizates at room temperature, known as natural aging, is due principally to a reaction between the rubber and oxygen[1]. Although aging is not identical with oxidation[2], the relation between these two phenomena provides a convenient means of comparison.

It is generally accepted that an absorption of approximately one per cent by weight of oxygen corresponds to the complete destruction of a vulcanizate with regard to its mechanical properties[1].

The Arrhenius curve of the reaction can be determined by measurements in the range 50–150° C. Here the rate of oxidation is such that a run can be completed in a convenient length of time. Using the graph obtained, the rate of oxidation may be determined by extrapolation.

Index of aging is here defined as the time required for the reaction of approximately 20 millimols of oxygen per mol of C_5H_8, *i.e.*, roughly one per cent on the weight of the rubber. If a relationship can be derived between this index of aging and the rate of aging determined by mechanical means, such data would be useful in calculating the resistance to aging of a given vulcanizate.

Dufraisse[3] used a manometric technique in his fundamental study of the function of inhibitors in various autoxidation reactions. The concept of inverse catalysis as cited by Moureu and Dufraisse in their exposition of the theory of antagonistic peroxides arose out of these investigations. Christiansen[4] showed that the reaction mechanism proposed was inadequate, and he proposed a chain reaction.

Dufraisse has constructed an apparatus which makes possible the simultaneous measurement of the rate of oxidation in 10–20 absorbers, and has shown the principal influence of a series of factors, such as combined sulfur, time and temperature of vulcanization, concentration of filler and inhibitor, etc. Ordinarily the measurements are performed in comparison with a standard sample, and the absolute values of the rates are not calculated[5].

By means of a similar manometric method, Williams and Neal[6] investigated acetone-extracted vulcanizates, and found a constant dp/dt corresponding to a zero-order reaction, which in turn was explained by the concept of a chain mechanism, without attempting a quantitative formulation. Similar measurements were carred out by Morgan and Naunton[7], who confirmed the zero order reaction for acetone-extracted vulcanizates, and concluded with the statement that the rates were in agreement with the Arrhenius equation. A chain reaction was described by Bäckström and Beatty[8], which gave a quantitative expression of the kinetics.

The value of these manometric measurements has been somewhat reduced through an investigation by Carpenter[9]. Carpenter determined the rates in

* Reprinted from *Acta Chemica Scandinavica*, Vol. 4, No. 3, pages 487–507 (1950).

a constant-pressure device and found that the rate of oxidation varied with the pressure of the oxygen in contradiction to the manometric findings, and, further, that the sample continued to oxidize at the same rate after reduction of the pressure of oxygen for a considerable time. This persistency of rate of oxidation is assumed as the possible explanation of the zero-order reaction found by the manometric method.

Shelton and Winn[2] stated an autocatalytic reaction on vulcanizates of GR-S. The initial phase of the reaction could be described by the superposition of a first-order reaction at active centers in the butadiene-styrene structure and a zero-order reaction with normal structures. The same kinetics were developed by Stafford[10] for irradiated rubber vulcanizates measured at constant pressure. On raw rubber, Le Bras and Salvetti[11] found more complicated variations of the rate of oxidation at constant pressure. Le Bras used a very interesting apparatus, in which the oxygen was prepared by electrolysis, a method which is not free from danger, as a trace of ozone might be expected in the electrolytic oxygen.

Unfortunately the determination and isolation of the peroxides in rubber is still an unsolved problem and, in consequence, the fundamental basis for the kinetic treatment of the problem is lacking. The theory proposed by Bolland and Gee[12] for the autoxidation of esters of linoleic acid, however, seems to be a very attractive explanation, which might be extended to the oxidation of rubber as mentioned by Mesrobian and Tobolsky[13]. According to Bolland and Gee, the initiation is performed by free radicals formed by thermal decomposition of the peroxide and termination by reactions between the radicals.

In a somewhat similar manner, Cole and Field[14] explain the oxidation of GR-S, where the free radical is formed through reaction of the diene complex with active oxygen. Termination by an inhibitor of the phenylnaphthylamine type is effected by reaction between the primary peroxide and the iminohydrogen atom in the inhibitor, whereby a new free radical with insufficient energy for chain propagation is formed.

In spite of the foregoing criticism of the manometric method, it shows some indisputable merits, namely, its simplicity and the ease with which multiple determinations are performed. In the following experimental part, therefore, we shall try to elucidate the possibilities of the method with respect of reproducibility of the results and for the empirical determination of the effects of antioxygenic agents and of copper and manganese soaps.

PREPARATION OF THE SAMPLES

All compounds were mixed on an ordinary laboratory mill with all precautions. The raw rubber was cut from the interior of a selected bale of smoked sheet rubber. Slabs were molded in a cavity in iron molds 200 × 100 × 2 mm. between two hard polished aluminum plates and immediately cooled in water after removal from the press. The slabs were cut into about 10 × 20 mm. pieces and crumbed by 4–5 passages through tight rollers on the mill. The crumbs were further disintegrated in a small mill furnished with helical blades, and the resulting powder was sieved to pass 100 per cent through 30 mesh and 0 per cent through 60 mesh. The surface of the samples was approximately 200–300 sq. cm. per cc., and the value was roughly determined by counting all gains in 1–10 mg. of powder weighed on a microbalance and evenly spread on a piece of millimeter paper.

THE ABSORBERS

Preliminary experiments were carried out in a modified Dufraisse absorber made of glass. The absorber was filled with oxygen by flushing from a tank 10 minutes. This method brought about difficulties in avoiding streaks in the grease used for the sealing of the ground-glass joints, which was turned 180° to close the connection with the atmosphere through corresponding channels in the glass stopper and the absorber joint. These difficulties are avoided in the absorber described below (Figure 1).

The absorber is fitted with a very carefully ground joint, 1, sealed with a proper amount of Cellogrease (Fisher Scientific Co.) on the upper third of the stopper. The reaction vessel, R, has a volume of 10 cc., and the capillary is 500 mm., with a bore of 0.8–1 mm. and a volume of 0.3–0.4 cc. The capillary extends 15 mm. into R, and is covered by the perforated microbeaker, 5. In the mercury reservoir the capillary is fixed in a rubber stopper with a smooth

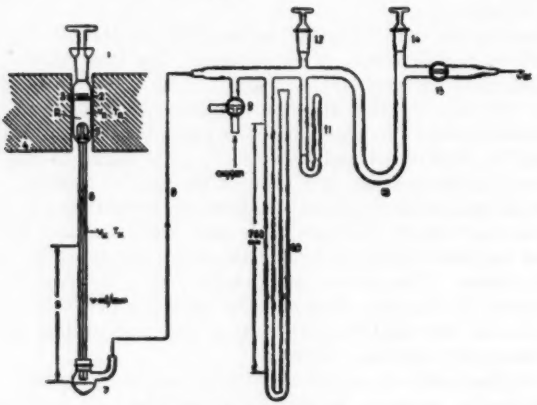


FIG. 1.—Oxygen absorber.

bore, moistened with very little glycerol. The position of the end of the capillary is adjusted to a few millimeters over the mercury surface. Two grams of rubber of the fineness mentioned is introduced into the absorber, and 0.3–0.4 gram of ascarite is placed over the sample in a microglass, 2, to absorb water and carbon dioxide. The absorber is evacuated and filled by oxygen from the tank by means of the manometer, 10–11, and the cocks 9–15. This process is repeated 4–5 times, each time reaching a moderate vacuum of about 2–5 mm. Hg. Finally the absorber is lowered in the mercury, applying a slight pressure on the stopper[1]. At the last filling with oxygen one may stop at a pressure 40–70 mm. below the barometric pressure, which forces the mercury to mount in the capillary, and the readings can take place immediately after heat equilibrium is reached. Heating of the absorbers is performed in holes drilled in an electrically heated and automatically temperature controlled aluminum-block, 4, in which the 10–20 parallel manometer can be placed. The temperature differential in the rubber sample is about 0.1–0.5° C, using a closely controlled heating current.

Measurements at temperatures below 50° C are made in the absorber shown in Figure 2. The capillary is 350 mm., with a lumen of 2 mm. Filling

with oxygen is performed by the same method described above, with the auxiliary system placed in the ground glass joint, g. The sealing liquid, ethyleneglycol, is stored in the funnel, h, and the cock, i, is opened after the final addition of oxygen and the glycol flows into e, thereby sealing the absorber. The funnel is then removed and the absorber placed in a water thermostat and is finally closed by means of the stopper with the cock i. By opening i and applying gentle suction by mouth, the glycol meniscus may be adjusted to any desired position in the capillary, d. The rate is here measured with close temperature control and without influence of fluctuations of the barometric pressure. The vapor pressure of glycol is 2 mm. at 35° C.

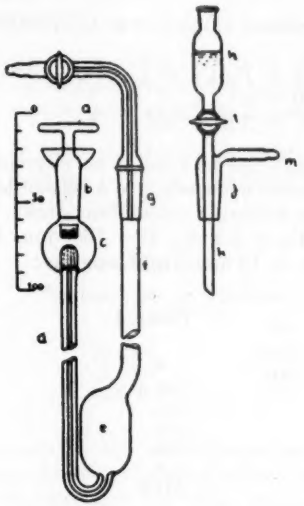


FIG. 2.—Closed absorber.

Most of the measurements were not conducted in absolute darkness but in very weak diffuse daylight.

CALCULATION OF THE RATE OF OXIDATION

With the symbols used in Figure 1 and volume of the capillary w cc. per mm., the amount of oxygen in the absorber is given by:

$$\begin{aligned} O_2 &= \text{p. f. } (V_R \cdot \perp_R + V_K^* \perp_K) \text{ mols} \\ f &= 273.2/760 \cdot 22392 = 1.605.10^{-6} \\ V_K^* &= V_K - s.w \\ \perp &= 1000/T \end{aligned}$$

and the pressure in the absorber:

$$p = B - s$$

where s is the height of the mercury column in the capillary, B the barometric pressure, V_K the total volume, and V_K^* the volume corresponding to s of the

capillary. By differentiation in respect to time h (hours) the rate is:

$$v = \frac{dO_2}{dt} = -f \cdot \frac{dp}{dt}[V_R \perp_R + \perp_K (V_K + w(2p - B))] \qquad (1)$$

v is expressed in moles of oxygen per hour and g C_5H_8, omitting the constant 10^{-8} in all quotations of rates of oxidation.

The condition for zero-order reaction is determined by integration of Equation (1), keeping v constant:

$$\frac{K}{t \cdot f} = -Ap - Dp^2 + C \qquad (2)$$

where K denotes the constant value of v at temperature T and the constants of integration are:

$$A = V_R \perp_R + \perp_K (V_K - wB)$$
$$B = w \cdot \perp_K$$
$$C = AB + DB^2$$

Consequently a straight line s–t relation corresponds to a slight decrease in v, and opposite the s–t curve concording to a zero-order reaction must be concave to the s-axis as the following calculation shows. Choosing $V_R = 9$ cc., $\perp_R = 3.7$, $\perp_K = 3.4$, $V_K = 0.4$ cc., $B = 760$ mm. Hg, $w = 0.0008$ cc. per mm., and dp/dt = const. = 10 mm. Hg/h, one has:

TABLE 1

s mm. Hg	v^s	t hours
0	591.6	0
100	583	9.89
200	574	19.63
300	565	29.22
400	556	38.67
500	547.9	47.97

v^s: rate of oxidation corresponding to s mm. Hg.

The column v^s is calculated from Equation (1), and it is seen that the rate decreases 7 per cent when calculated on v^0, which is insignificant compared with the normal accuracy of the method. The column t is calculated at v = 591.6 = const. from Equation (2);

$$368.6 \cdot t = -32.59 \cdot p + 0.0027\, p^2 + 26339$$

and the curvature of the s–t lines becomes very small.

For the absorber Figure 2 kept at constant temperature T, the rate is calculated from:

$$v = f \cdot \perp \frac{dp}{dt}\left[V_0 + \frac{w}{b}(2p - B)\right] \qquad \text{(Approx. 3)}$$

where V_0 denotes the combined volume of absorber and capillary corresponding to $s = 0$ and b the ratio of the density of glycol at $T°$ and mercury at 273° ($b = 7.91 \cdot 10^{-2}$ at 35° C).

The readings of t, s, B and T_K are tabulated and the s–t curve is plotted graphically.

RATE OF OXIDATION OF A STANDARD VULCANIZATE

WITHOUT ADDITION OF ANTIOXYGENIC AGENT

As a typical fast oxidizing vulcanizate a DPG-vulcanizate with the following formula was used throughout the investigation:

Smoked sheet rubber	100	100
Sulfur	1.5	1.5
Diphenylguanidine	1.5	1.5
Zinc oxide	10	10
Whiting	106	104
Carbon black	3	3
Antioxygenic agent	—	2

Vulcanization unless otherwise stated 15 min. at 152° C
Vulcanizates without antioxygenic agent are termed −
with antioxygenic agent are termed +

All the rates cited in the following tables are rates corresponding to $s = 0$: the initial rate computed from the s–t curve. In Table 2 are collected some data concerning the purity of the fillers used:

TABLE 2

PERCENTAGES OF METALS

Filler	Cu	Mn	Fe
Danish whiting	0.0004	0.01	0.1
Winnofil (ICI)	0.0003	0.007	0.08
Zinc oxide	0.005	nil	nil

Though all measurements on the vulcanizates were conducted with great care, with powders of approximately the same surface, it will be seen from Table 3 that it is impossible to reproduce the value of v. The reproducibility in double or multiple runs, using the same samples, is well established at about ±5–10 per cent, but changing to a new mix and using exactly the same ingredient yields results which differ widely. This is the case for the three samples 4620C, 47161B and 4823 all with Danish whiting, of which 4620 is slow and 4823 fast oxidizing, and 47161 gives an Arrhenius line of a different slope. One must be content with locating an upper and lower line for the area in which the vulcanizate by chance will locate itself, and the limitation is almost given by the ⊥-log v-lines for 4620C and 4823. The purity of the whiting does not seriously affect the rates, as shown by 4839 containing the pure precipitated stearic acid-coated calcium carbonate from ICI (Winnofil) placed intermediately in the interval. The sample 4852 is made from washed and vacuum-dried smoked sheet rubber from the interior of a bale. This process would be expected to remove some of the natural antioxidants in the rubber: nevertheless 4852 is slow oxidizing at the lower limit of the interval.

All graphs of s–t are strictly linear up to 200–300 mm. Hg at temperatures below 100° C, and in some cases graphs with a slight increase in ds/dt occur, *i.e.*, almost zero-order reaction. At higher temperatures (120–140° C) the curves start as straight lines, but at 100–200 mm. Hg the ds/dt value decreases rapidly. Rates above 150,000 are not realized, even with samples to which had been added a considerable amount of copper stearate. Above 100° C the

TABLE 3

INITIAL RATES OF OXIDATION FOR VULCANIZATES WITHOUT ANTIOXYGENIC AGENT
(mols O_2 per hour and g C_4H_8 ($\pm 10^6$))

	No. of mix	4620 C	47161 B	4823	4839	4852
	Rubber	SS[1]	SS[1]	SS[1]	SS[1]	Washed SS
	Filler	Whiting[2]	Whiting[2]	Whiting[2]	Winnofil[3]	Whiting[2]
°C	Surface (sq. cm. per cc.)			186	213	198
25	—	9.4	—	—	—	—
27	—	—	—	22.3	—	—
31.7	—	18.6	—	—	—	—
33.0	—	—	27.7	—	—	—
34.5[4]	—	—	—	—	20.3	21.1
40.7	—	37.0	—	—	—	—
45.6	—	—	132	—	—	—
49.3	—	120	—	—	—	—
57.5	—	—	477	—	—	—
59.5	—	—	—	671	603	485
60.4	—	340	—	—	—	—
69.4	—	—	1 680	—	—	—
74.4	—	—	—	2 860	—	—
79.5	—	—	3 800	—	1 904	1 640
89.4	—	—	—	9 100	—	—
100.4	—	—	—	18 500	11 400	6 900
121.3	—	—	44 000	—	—	—
	$\log_{10} v^{0.5}$	7.809 $-4.436 \cdot \perp$	9.844 $-5.016 \cdot \perp$	8.371 $-4.504 \cdot \perp$	8.874 $-4.778 \cdot \perp$	7.711 $-4.414 \cdot \perp$
	H^6 mols/mols·sec	14.00	18.68	15.30	16.45	13.77
	Q^6 kcal	20.4	23.1	20.7	22.0	20.3

[1] Standard smoked sheet.

[2] Washed Danish whiting.

[3] Stearic acid-coated precipitated calcite from J. C. J.

[4] Measured in the closed absorber (Figure 2).

[5] Derived by regression analysis.

[6] Arrhenius equation: $\ln v^0 = H\frac{Q}{R \cdot T}$

diffusion becomes a controlling factor, and it is difficult to prepare samples with surfaces exceeding about 300 sq. cm. per cc. Due to the lack of consistency, it is impossible to determine the kinetic constants with reasonable accuracy, but the energy of activation (mean value from Table 3) is about 21 kcal. and the constant H about 15.6 (mol./mol.sec). Finally we can calculate a mean Arrhenius line given by:

$$\log_{10} v = 8.52_3 - 4.63_0 \cdot \perp$$

which will be used as an average standard in discussing retardation by antioxygenic agents and acceleration by copper and manganese soaps in the following measurements.

COMPOUNDS WITH COPPER AND MANGANESE

To the base formula were added various percentages of copper stearate (containing 9.4 per cent copper) and manganese oleate (about 1 per cent manganese). The tensile strength and modulus of the vulcanizates are definitely reduced, and the elongation increases, as the figures in Table 4 show.

TABLE 4

TENSILE PROPERTIES
(Sample 47·161 B)

Addition (%)	*R·T* Antioxygenic agent (parts)	TB[1] (kg. per sq. cm.)	M_3[2] (kg. per sq. cm.)	EB[3] (%)
nil	—	152	54	510
0.01 Cu[4]	—	157	57	510
0.05 Cu[4]	—	134	44	540
0.01 Mn[5]	—	132	38	520
0.05 Mn[5]	—	85	14	640
nil	2[6]	163	55	520

[1] Tensile strength at break.
[2] Modulus at 300% elongation.
[3] Elongation at break.
[4] As copper stearate.
[5] As manganese oleate.
[6] Two parts per 100 smoked sheet (Antioxygène A, Francolor).

The addition of 0.01 per cent of copper causes a small increase in tensile strength and modulus, presumably through cross-linking of oxygen. The chain scission is very clearly shown at the higher copper concentration and in all cases with manganese. These samples deteriorate very fast at room temperature in darkness, and surface tackiness develops in a few days, while the tackiness of copper containing specimens appears after some weeks. The *s–t* graphs are all very characteristic, with pronounced increase in ds/dt in many cases

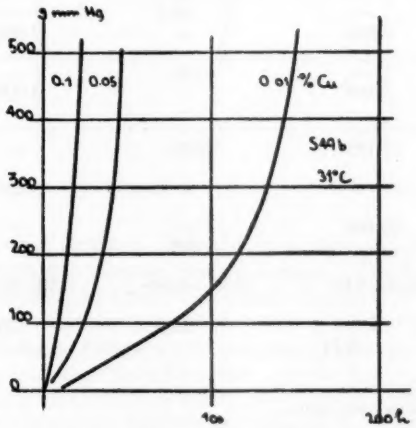


FIG. 3.—*s-t* for crepe (without antioxygenic agent + Cu).

TABLE 5

INITIAL AND FINAL RATES OF OXIDATION OF PALE CREPE VULCANIZATES WITH CU AND NO ADDITION OF ANTIOXYGEN[1]

(mols. O per hour and g. $C_5H_8 \cdot (\pm 10^8)$)

Sample	% Cu[2]	° C	initial rate $\sim_s = 0$[3]	final rate $\sim_s = 500$
4620 G	nil	31.0	36.4± 1.6	—
	—	49.4	253 ± 23	—
	—	59.6	699 ± 21	—
4620 H	0.01	31.0	88.7± 1.2	696±1
	—	49.4	545 ± 15	—
	—	59.6	1 270 ± 46	14 800±5 500
4620 I	0.05	49.4	980 ± 24	—
	—	59.6	3 900 ±285	19 280±125
4620 J	0.1	49.4	1 520 ± 90	—
	—	59.6	5 000 ± 45	33 750±1 650

[1] Two mm. slabs vulcanized 60 min. at 142° C, surface of powder 280 cm.²/cm.³ All figures mean value of duplicate runs.
[2] As copper stearate.
[3] s in mm. Hg.

TABLE 6

INITIAL RATES OF OXIDATION FOR VULCANIZATES WITH ADDITION OF COPPER AND MANGANESE WITHOUT ANTIOXYGENIC AGENT

(mols. oxygen per hour and g. smoked sheet ($\times 10^8$))

No. of mix	47 178	48 24	4825	4825
% addition	0.01 Cu[1]	0.01 Cu[1]	0.01 Mn[2]	0.01 Mn[2]
Condition of sample	Aged 2 mths.	Fresh	Fresh	Fresh
Surface (sq. cm. per cc.)	280	260	30[3]	70[4]
° C	—	—	—	—
27.0	—	48.8	—	—
28.0	2 300	—	2 060	—
38.0	—	188	—	—
38.9	5 400	—	3 000	—
41.0	—	—	—	18 000
57.5	17 100	2 070	—	69 200
58.8	—	—	9 400	—
69.4	39 400	—	—	—
74.4	—	8 200	—	—
$\log_{10} v^{\circ}$	$5.51-3.06 \cdot \perp$	$10.33-5.00 \cdot \perp$	$2.52-2.18 \cdot \perp$	
Q kcal	14.1	23.0	10.0	—
H	8.71	—	—	—

[1] As copper stearate.
[2] As manganese oleate.
[3] Cut with razor in 2 × 1 mm. slabs.
[4] Crumbed on the mill.
[5] By regression.

after a straight line initial curve, recalling the well known autocatalytic process with a period of induction.

A set of samples with pale crepe instead of smoked sheet rubber was typical in this respect, as would be anticipated from the lower content of natural antioxygenic substances in the crepe. The s–t graphs are shown in Figure 3 and the rates tabulated in Table 5, which in addition shows the reproduction of duplicate determinations. The base vulcanizate coincides very closely with 4823 (Table 3). The graph for 4620 H with 0.01 per cent copper proceeds as a

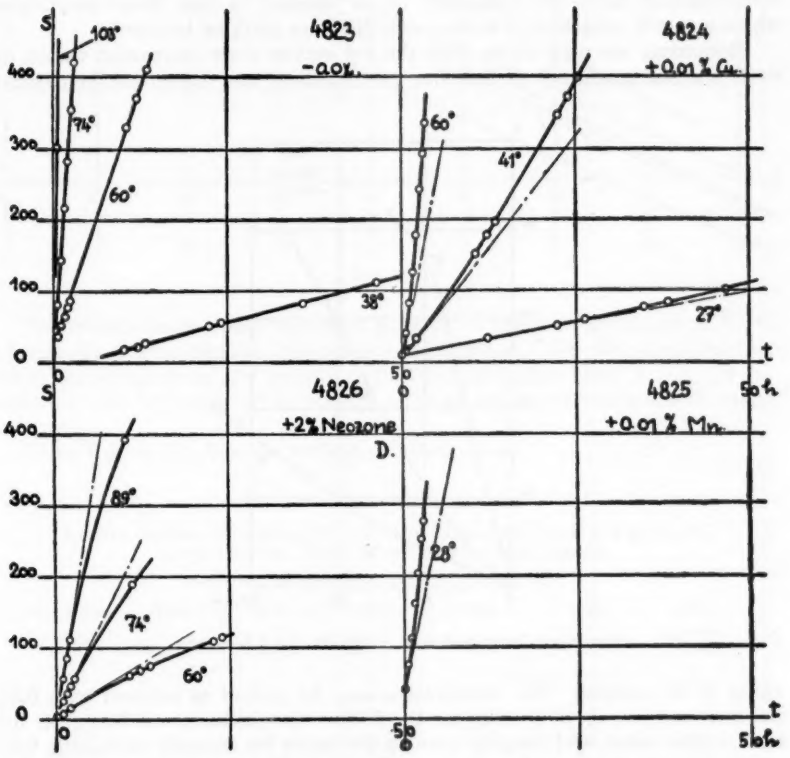


FIG. 4.—s–t for smoked sheet ± with antioxygenic agent; Mn and Cu as indicated. ± Mn and Cu.

straight line for the first 80 hours: then the slope increases at an even rate to 120 hours, after which the increase becomes rapid. The figures in Table 5 show that the final rates may exceed the initial rates by 5–6 units.

The corresponding rates for smoked sheet are given in Table 6, and some typical s–t graphs shown in Figure 4. The autocatalytic course is still evident, though much less pronounced than for crepe. At the higher temperature, the s–t graphs have a point of inflection, the reason for which is obscure, as an inefficiency of diffusion might not be expected (Figure 5).

The freshly prepared sample 4824 has constants much like the base compound, in accordance with the analogy in the tensile strengths. If the sample is subject to aging at room temperature, the rate of oxidation increases very much as the sample of 48 178, aged 2 months, shows. In addition the Arrhenius line has much less slope.

Sample 47 178 finally was measured at the time where the transition from a dry powder to a very tacky sponge took place, and during this transformation, which lasted six days, the initial rate was increased from 2300 to 5300 (at 28° C). Finally the sample formed a hard mass, with an aromatic and sharp smell. The measurements show the possibility of an increase in rate under conditions where a severe reduction of surface and diffusion must be assumed.

Resuming, we may stress that the s–t curves show increasing values of ds/dt and the magnitude of the rates are undefined, and depend on the natural

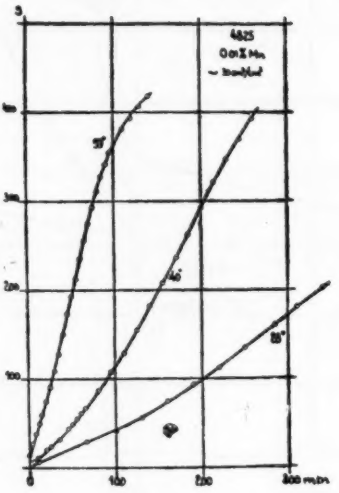


FIG. 5.—s-t for smoked sheet + 0.01 Mn, 2 × 1 mm. slabs.

aging of the sample. The acceleration may be judged as follows: with 0.01 per cent copper, about 5 units for the fresh vulcanizate, about 200 units for aged vulcanizates, and ranging towards 500 units for samples containing 0.01 per cent manganese.

THE EFFECT OF ANTIOXYGENIC AGENTS

The graphs of the s–t values all show a very pronounced decrease in ds/dt, and the shape of the curves resembles those cited of Carpenter[9] and Milligan and Shaw[15]. The order of reaction is in many cases approximately unity. Though the determination of the initial rate is not very well defined because of the geometry of the s–t curve, the reproduction is very satisfying, and all measurements of vulcanizates containing common antioxygenic agents, as phenyl-β-naphthylamine (PBN), are concentrated at the same Arrhenius line with good accuracy (A–A in Figure 6).

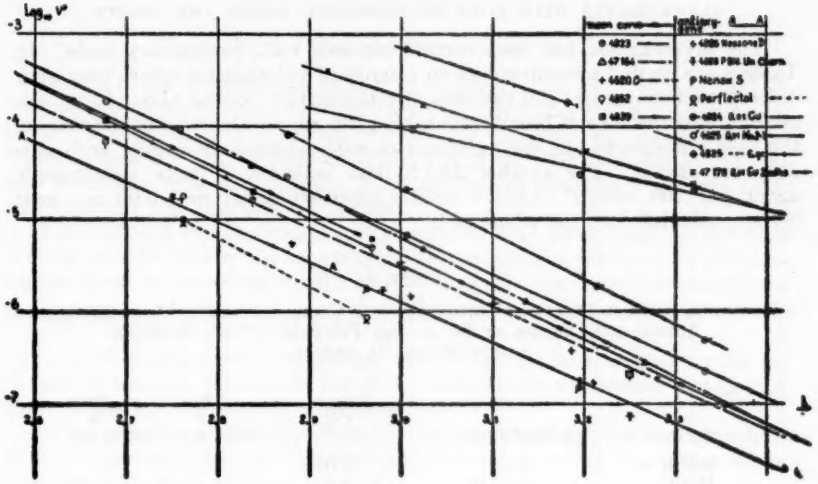


FIG. 6.

The retardation is rather modest, *e.g.*, at 25° C about 2.6 units and at 70° C 3.4 units for phenyl-naphthylamines and aldolamines. For the more effective antioxygenic agents of the phenylene-diamine aryl-substituted types, the retardation may be judged to be about 7 units at lower and intermediate temperatures.

Table 7 gives the data for various + vulcanizates.

TABLE 7

INITIAL RATES OF OXIDATION FOR VULCANIZATES WITH 2 PARTS OF ANTIOXYGENIC AGENTS PER 100 SMOKED SHEET

(mols. oxygen per hour and g. C_5H_8 ($\times 10^8$))

No. of mix	47163	4833	4826	4828	4829	4832
Antioxygenic agent	Antioxygène-A[1]	Perflectol[2]	Neozone-D[3]	PBN[4]	Nonox-S[5]	Agerite White[6]
° C	—	—	—	—	—	—
34.9	—	—	—	7.4	—	—
38.0	—	—	17.1	—	—	—
39.9	—	—	—	17.0	15.1	—
59.5	—	—	147	—	—	—
64.4	—	87	—	171	178	—
68.2	263	—	—	—	—	—
74.4	—	—	550	—	—	—
79.8	530	—	—	—	—	—
88.9	—	1 010	—	—	1 760	1 025
89.4	—	—	1 610	—	—	—
90.6	—	—	—	1 700	—	—
103.3	—	—	3 125	—	—	—

Mean for 47163, 4826—28—29, $\log_{10} v^\circ = 7.11 - 4.33 \cdot \perp$, $Q = 19.9$, $H = 12.4$.

[1] Phenyl-α-naphthylamine ~ PAN.
[2] Blend of Flectol-H, an acetone-aniline condensation product, and *N,N'*-diphenyl-*p*-phenylenediamine.
[3] Phenyl-β-naphthylamine ~ PBN.
[4] From United Chemicals, Praha.
[5] Unknown composition.
[6] *N,N'*-di-β-naphthyl-*p*-phenylenediamine.

VULCANIZATES WITH BOTH ANTIOXYGENIC AGENT AND COPPER

The investigation has been carried out only on a preliminary scale. In Table 8 are quoted measurements on a series of vulcanizates which were very difficult to disintegrate, and consequently the surface became about 50 sq. cm. per cc. For the sake of brevity the table gives simply the ratio of the rates of the base vulcanizate and the vulcanizates with addition of copper and antioxygenic agents. The symbol 2AAN/0.05 indicates 2 parts antioxygenic agent per 100 rubber (AAN = aldol-α-naphthylamine) and 0.05 per cent copper, calculated on the whole mix.

TABLE 8

RATIOS OF INITIAL RATES OF OXIDATION FOR COMBINATIONS OF ANTIOXYGENIC AGENT AND COPPER AT 60° C AND POWDERS WITH A SURFACE ABOUT 50 SQ. CM. PER CC.

Mix no.:	Antiox.[2]/% Cu	$\Phi = \frac{v°_{Aox.Cu}}{v°_{0}}$	$\Phi' = \frac{\Phi_L}{\Phi}$ (0.01% Cu)	$\Phi'' = \frac{\Phi_M}{\Phi}$ (0.05% Cu)
4620K	0 /0	1.00	—	—
4620L	0 /0.01	+ 5.8	—	—
4620M	0 /0.05	+24	—	—
4620N	2PBN[3]/0	− 0.29	—	—
4620O	2AAN[4]/0	− 0.28	—	—
4620P	4PBN /0	− 0.28	—	—
4620Q	4AAN /0	− 0.32	—	—
4620R	2AAN /0.01	+ 2.6	2.2	—
4620S	2AAN /0.05	+ 6.6	—	3.6
4620Y	4AAN /0.01	+ 2.7	2.1	—
4620V	4AAN /0.05	+ 6.0	—	4.0
4620T	2PBN /0.01	+ 1.5	3.9	—
4620U	2PBN /0.05	+ 2.9	—	8.2
4620Æ	4PBN /0.01	+ 2.1	2.8	—
4620X	4PBN /0.05	+ 4.7	—	5.1

[1] Φ' and Φ'' are a relative measure of the retarding power of the antioxygenic agents at a copper content pf 0.01 and 0.05, respectively.
[2] Parts of antioxygenic agent per 100 smoked sheet.
[3] PBN ~ phenyl-β-naphthylamine } from I. G. Farben.
[4] AAN ~ Aldol-α-naphthylamine }
+ Denotes acceleration,—retardation.

The retarding effect of the antioxygenic agents is most pronounced at the high concentration of copper, as indicated by the proportions ϕ', and ϕ'' in Table 8. An increase of the percentage of antioxygenic agent above 2 parts per 100 rubber shows no effect as measured by the initial rate of oxygen absorption. PBN seems to give a somewhat greater protection against copper than does AAN, although the possibility of formation of complexes with copper has been stressed in the case of AAN by Kirchhof[16]. Jones and Craig[17] demonstrated the superiority of the aryl-substituted phenylenediamines in combination with copper, a point of view which we hope to treat in a later communication. Due to the forementioned instability of vulcanizates containing copper, the measurements cited in Table 8 are not quite consistent, *e.g.*, 2 parts PGN causes greater relative retardation than 4 parts in the samples with both 0.01 and 0.05 per cent copper.

APPENDIX

SOME PRELIMINARY AGING TESTS

Several of the samples were aged in circulating air at 70°, 95°, and 130° C. The aging tests were carried out with dumbbell specimens, cut from slabs 2 mm. thick. The width of the narrow neck of the specimen was exactly 5 mm. Tensile strength (TB), elongation (EB) at rupture, and modulus at 300 per cent elongation was determined. Measurements of the moduli showed complications and are consequently omitted.

The values of tensile strength and elongation were plotted against the time in days, and the slope of the zero tangent determined graphically. In calculating the slope as percentage of the zero value, we denote these decrease figures as N_{TB} and N_{EB}, defined by $N_x = -\frac{\partial x}{\partial t}\cdot\frac{100}{x}$.

From the aging curves was further determined the time elapsed for the reduction of the zero value to 50 per cent, which figures are termed as $t_{\frac{1}{2}TB}$ and $t_{\frac{1}{2}EB}$. Table 9 gives some data, measured at 70° C.

In the column v_{70} the rate of oxidation is calculated from the average values of the Arrhenius lines. ϕ^{v° denotes the ratio v_-/v_+ + and ϕ_{Ag} is the corresponding ratio for N and $t_{\frac{1}{2}}$.

It is seen that the retardation by antioxygenic agents is very consistent, whether measured as ratios of rates of oxidation or as ratios of aging, judged

TABLE 9

DECREASE IN VALUES BY AGING AT 70° C IN CIRCULATING AIR

Mix. no.	Antioxygenic agent	N_{TB} (% per day)	N_{EB} (% per day)	$t_{\frac{1}{2}TB}$ (days)	$v^\circ_{77^\circ}$	$\Phi V^\circ_{70^\circ}$	Φ_{Ag} Φ_{TB}	Φ_{Ag} Φ_{EB}	Φ_{Ag} $\Phi_{\frac{1}{2}TB}$
47 161 B	÷	9.9	0.71	11.2	—	—	—	—	—
48 23	÷	9.7	1.30	5.2	—	—	—	—	—
48 30	÷	6.4	0.69	10.3	—	—	—	—	—
Average	÷	8.7	0.90	8.9	1 070	—	--	—	—
47 162	PBN I. G.[1]	2.0	0.43	41	—	—	—	—	—
47 165	Antioxygène MC[1]	1.5	0.11	50	—	—	—	—	—
48 26	Neozone D[1]	3.4	0.54	34	—	—	—	—	—
48 28	PBN[2]	4.0	0.62	34	—	—	—	—	—
Average	+PBN	2.7	0.43	40	310	−3.4	−3.2	−2.1	−4.4
47 163	Antioxygène A[3]	2.2	0.40	(50)	—	—	−3.9	−2.3	—
47 164	Antioxygène INC[4]	—	0.36	(54)	—	—	—	−2.5	—
48 29	Nonox-S[5]	2.0	0.50	48	—	—	−4.4	−1.8	−5.4
48 31	Flectol-H[6]	2.6	(0.78)	(33)	—	—	−3.3	—	—
48 32	Agerite White[7]	2.4	0.42	(54)	—	—	−3.6	−2.1	—
48 33	Perflectol[8]	1.4	0.34	—	160	−6.3	−6.2	−2.6	
48 24	−with 0.01% Cu	55	7.7	1	5 500		+5.1	+6.3	+8.6 +8.9

(+: acceleration)
(−: retardation)

$\Phi v^\circ = \frac{v^\circ_-}{v^\circ_+}$ or $\frac{v^\circ_+/Cu}{v^\circ_+}$; $\Phi_{Ag} = \frac{N\ -}{N\ +}$ or $\frac{t_{\frac{1}{2}}\ +}{t_{\frac{1}{2}}\ -}$ +: vulcanizates without antioxygen
−: vulcanizates with antioxygen

[1] PBN.
[2] From United Chemicals, Praha.
[3] Phenyl-α-naphthylamine.
[4] Aldol-α-naphthylamine.
[5] Unknown composition.
[6] Acetone-aniline condensation product.
[7] *N,N'*-di-β-naphthyl-*p*-phenylenediamine.
[8] Blend of Flectol-H and *N,N'*-diphenyl-*p*-phenylenediamine.

by tensile strength. The elongation determines a lower retardation and the $t_{\frac{1}{2}}$ value a higher retardation. Ordinary antioxygenic agents, such as Flectol-H and naphthylamines, give a retardation of 3–4 units; the more effective substituted *p*-phenylene-diamines give a greater retardation about 6–7 units. The value for Agerite White must be discarded as it is expected that this antioxygenic agent and Perflectol should be equal.

The effect of temperature is illustrated in Table 10, which shows measurements at 70°, 95°, and 130° C. The data show that the retarding effect decreases with increasing temperature. The coefficients of temperature are not consistent, *i.e.*, are too low at 95°/130°, possibly because of insufficient diffusion.

TABLE 10

A. RETARDATION AT 70°, 95°, AND 130° C

° C	Mix. no.	Antioxygenic agent*	N_{TB} % per hour	$\Phi = \frac{N-}{N+}$	$v°$
70°	4830	÷	0.266	—	1 070
	4831	Flectol-H	0.108	2.5	310
	4833	Perflectol	0.058	4.6	160
95°	4830	—	3.7	—	8 900
	4831	—	2.7	1.4	2 240
	4833	—	1.1	3.4	—
130°	4830	—	13.3	—	—
	4831	—	6.4	2.1	—
	4833	—	5.9	2.3	—

B. TEMPERATURE COEFFICIENTS

Mix. no.	$\Phi' = \frac{N_{T1}}{N_{T2}}$ 95°/70°	130°/95°
4830	13.9	3.6
4831	25	2.4
4833	19	5.3
$v°_{\div}$	8.3	—
$v°_{+}$	7.2	—

* Two parts per 100 smoked sheet.

Better figures would possibly result by the use of normal rings whereby the tensile properties are more strictly defined. The use of slabs is, however, very practical, as little area of rubber samples is demanded for the performance of the tests.

Calculating the *index of aging* from the rates of oxidation at 70°, we find 1.2 days for the −-vulcanizate and 4.2 days for the +-vulcanizate, *i.e.*, about one-tenth of the measured $t_{\frac{1}{2}TB}$ values, quite a reasonable magnitude, taking into account the difference in surface.

When data from the course of the natural aging are available the comparison of the N values and the v-values at room temperature can be computed, by means of which we shall obtain a final judgment of the significance of the aging indices.

SUMMARY

An apparatus is described for the measurement of the rate of the oxidation of rubber vulcanizates by a simple technique. New formulas for calculating the rate from pressure and time readings are derived (see Equations 1 and 2).

For a diphenylguanidine vulcanizate, some typical s–t graphs[18] are shown. If no antioxygenic agent is added, the s–t function becomes a straight line (in some cases with a slight increase in ds/dt)indicating approximately a zero-order reaction. Duplicate runs agree very well (±5 per cent), but reproduction of the rates of samples from parallel mixes from the same base smoked sheet is very poor.

With addition of two parts of antioxygenic agent per 100 smoked sheet, the s–t graphs show a very pronounced decrease in slope, and the order of the reaction is between zero and one. The reproduction is very good in all cases, and the measurements of mixes containing common antioxygenic agents yields the same Arrhenius curve for the initial velocities.

Vulcanizates containing 0.01 per cent of copper or manganese as soaps are very unstable. The s–t curves have increasing slopes in some cases after a straight-line initial course. The rate is here a rather undefined property, with a rapid increase with the age of the sample.

The rates of oxidation for powders of an approximate surface area about 300 sq. cm. per cc. are expressed by the following equations[19]:

Without antioxygenic agent	$\log_{10} v = 8.52 - 4.63 \cdot \perp$
With two parts of antioxygenic agent	$\log_{10} v = 7.1 - 4.33 \cdot \perp$

(See Tables 3, 5, 6, 7 and 8.)

Preliminary aging tests gave a factor for the retardation of the rates by ordinary antioxygenic agents which coincided with the retardation determined by the initial rates of oxidation.

Common antioxygenic agents retard the rate of oxidation 3–4 times and aryl-substituted phenylendiamines 6–7 times.

The acceleration of the rate of oxidation by copper and manganese soaps (especially in samples aged for short times at room temperature in darkness) may amount to 200–500 times the velocity of the base vulcanizate. Calculated in molar concentrations, the accelerating power of copper and manganese is about 1 300 times greater than the retarding power of phenyl-β-naphthylamine.

ACKNOWLEDGMENT

Finally I wish to thank my firm A/S Nordiske Kabel- og Traadfabriker for permission to publish this work, and Professor J. A. Christiansen and Mr. J. S. Hunter and Dr. Morgan (Monsanto Chemicals Ltd.) for some very valuable help during the work.

REFERENCES

[1] Kohman, *J. Phys. Chem.* **33**, 226 (1929); RUBBER CHEM. & TECHNOL. **2**, 390 (1929).
[2] Shelton and Winn, *Ind. Eng. Chem.* **38**, 71 (1946); RUBBER CHEM. & TECHNOL. **19**, 696 (1946).
[3] Dufraisse, "Traité de Grignard," 1936, p. 1147.
[4] Christiansen, *Trans. Faraday Soc.* **24**, 714 (1928).
[5] Dufraisse, RUBBER CHEM. & TECHNOL. **11**, 268 (1938); Dufraisse and Le Bras, *Proc. Rubber Technol. Conf. London*, 1938, p. 535; RUBBER CHEM. & TECHNOL. **13**, 604 (1940).
[6] Williams and Neal, *Ind. Eng. Chem.* **22**, 874 (1930); RUBBER CHEM. & TECHNOL. **3**, 678 (1930).
[7] Morgan and Naunton, *Proc. Rubber Technol Conf. London*, 1938, p. 599; RUBBER CHEM. & TECHNOL. **12**, 235 (1939).
[8] Bäckström and Beatty, *J. Phys. Chem.* **35**, 2530 (1931).
[9] Carpenter, *Ind. Eng. Chem.* **39**, 187 (1947); RUBBER CHEM. & TECHNOL. **20**, 728 (1947).

[10] Stafford, *Proc. 2nd Rubber Technol Conf. London*, **1948**, p. 94; RUBBER CHEM. & TECHNOL. **23**, 404 (1950).
[11] Le Bras and Salvetti, *Proc. 2nd Rubber Technol. Conf. London*, **1948**, p. 123; RUBBER CHEM. & TECHNOL. **22**, 690 (1949).
[12] Bolland and Gee, *Trans. Faraday Soc.* **42**, 236 (1946); RUBBER CHEM. & TECHNOL. **20**, 609 (1947).
[13] Mesrobian and Tobolsky, *J. Polymer Soc.* **2**, 463 (1947).
[14] Cole and Field, *Ind. Eng. Chem.* **39**, 174 (1947); RUBBER CHEM. & TECHNOL. **20**, 747 (1947).
[15] Milligan and Shaw, *Proc. Rubber Technol. Conf. London*, **1938**, p. 537; RUBBER CHEM. & TECHNOL. **12**, 261 (1939).
[16] Kirchhof, *Kautschuk* **6**, 119 (1930); **7**, 7 (1931); **9**, 70 (1933); RUBBER CHEM. & TECHNOL. **4**, 239 (1931); **6**, 391 (1933).
[17] Jones and Craig, *Ind. Eng. Chem.* **23**, 23 (1931); RUBBER CHEM. & TECHNOL. **4**, 108 (1931).
[18] Here s is the height of the mercury (mm.) at time t. The slope, $ds/dt = -dp/dt$.
[19] The factor $\perp = 1000/T$.

ALFIN CATALYSTS AND THE POLYMERIZATION OF BUTADIENE *

AVERY A. MORTON

MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASS.

The alfin catalysts are special combinations of sodium salts, one from an alcohol and the other from an olefin, which have unique properties as polymerizing agents for butadiene and similar compounds. In order to appreciate clearly this account of the discovery, special properties, problems, and possible mechanisms, it is helpful to keep in mind two important principles which apply to all reactions and reagents in the field of organosodium compounds, whether for polymerization or for some simpler process. One is the tendency for organosodium reactions to consist of multiple steps which tumble over each other as if in cascades until the end is reached. The other is the control which inorganic components of the reagent and other inorganic salts exert on the process, a circumstance that arises from the fact that the reagents are insoluble aggregates of ions, somewhat as in the crystal of sodium chloride, and are not fully dispersed in a solvent, so that the ions act separately. An understanding of these points is essential for anyone who works with these extremely reactive reagents which operate only in heterogeneous processes.

DISCOVERY OF THE CATALYST

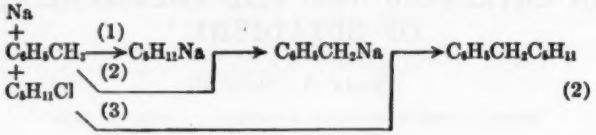
The importance of the two ideas mentioned above is better understood with a background of the chemistry of organosodium compounds. For example, in the Wurtz reaction, long held as the most typical activity of sodium in organic chemistry, amyl chloride with metallic sodium yields either decane or the pentane-pentene pair so rapidly that for a long time the majority of chemists regarded the process as the random behavior of free radicals released in the reaction mixture. Now, however, it is known to consist principally of two distinct phases (Equation 1) and can be interrupted after the first one[1] if the

(1)

amyl chloride is added dropwise to sodium sand while it is vigorously stirred in pentane. With the higher-speed stirring apparatus[2] developed especially for these heterogeneous systems, and with other factors, such as temperature and time, under control, as high as 95 per cent of the chloride can be accounted for as amyl-sodium, a remarkable yield for such an extremely reactive intermediate.

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 42, No. 8, pages 1488–1496, August 1950. This paper was presented in large part before the Division of Rubber Chemistry at the 116th Meeting of the American Chemical Society, Atlantic City, New Jersey, September 18–23, 1949. A part is from a paper presented at a Symposium on Organometallic Compounds held by the Division of Physical and Inorganic Chemistry at the 113th Meeting of the American Chemical Society, Chicago, April 19–23, 1948.

An in-between step is inserted when this process is carried out in toluene. In seemingly one operation the process cascades through three levels to an alkylated benzene in good yield (Equation 2). Here, too, the process can be interrupted at intermediate steps[3].



(2)

With the aid of this amylsodium intermediate and similar ones, the second phase[4] of the Wurtz reaction can be shown to be determined by the inorganic components of the reagents. For instance (Table I), the reactions of *n*-octylsodium with three different methyl halides are different, despite the fact that in each instance the hydrocarbon components are identical. And the reaction of such reagents with alkyl halides in a common disproportionation yields the alkane from the organosodium component and the alkene from the halide (a

TABLE I

REACTION OF *n*-OCTYLSODIUM WITH METHYL HALIDES

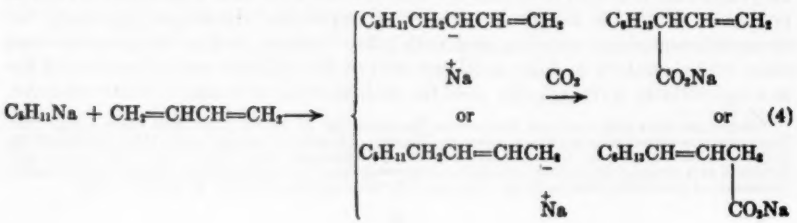
	Percentage yields of different products		
n-Octylsodium with	Wurtz, nonane	Disproportionation, octene and octane	Dimerization, hexadecane
CH_3Cl	22	18	7
CH_3Br	21	10	27
CH_3I	6	0	50

similar reaction was independently observed by Whitmore and Zook[5]), as illustrated in Equation 3 for one of the reactions studied.

$$C_5H_{11}Na + C_6H_{13}Cl \rightarrow C_5H_{12} + C_6H_{12} + NaCl \qquad (3)$$

In all the above, we see a succession of orderly chemical steps which are subject to control by inorganic components rather than let loose to random behavior. With care the separate steps can be sorted and examined separately. In particular, also, we have at hand an extremely active reagent, amylsodium, capable of reactions not found with the more common magnesium and lithium reagents.

For the reaction of this organosodium compound with butadiene[6], the technique of dropwise addition of one reagent to a large excess of the other, which had proved so successful in the study of the Wurtz reaction, was applied in the hope that, here too, intermediate early phases could be trapped[6]. The process, represented in Equation 4, could be 1,2- or 1,4- and a decision was to

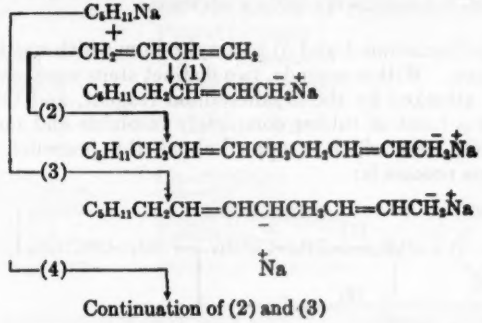


be made by carbonation and subsequent location of the carboxyl group. Ziegler's work[7] would cause the prediction that the product would be largely 1,2-. Of course, the sodium ion might be in either position without regard to the manner of addition, inasmuch as the system should display allylic isomerism or resonance as shown for the latter case by the formula

$$[C_5H_{11}CH_2\bar{C}HCH{=}CH_2 \longleftrightarrow C_5H_{11}CH_2CH{=}CH\bar{C}H_2]\overset{+}{N}a$$

However, in any subsequent reaction with carbon dioxide, alkyl halide, or diene the behavior is as if the sodium ion affected a specific carbon.

A small amount of acid 1,4-product was indeed isolated, and ozonization indicated that the larger amount was 1,2-, but the really important facts were in line with the two principles given above, namely, the occurrence of multiple or cascading reactions and control by inorganic components. (Inorganic components refer to all the ions, salts, or atoms present in the aggregate, exclusive of the hydrocarbon components.) One multiple reaction[8] started with addition of amylsodium to butadiene, continued by addition of the adduct to another molecule of diene, and then followed with metalation, after which repetition of the phases led to products of higher molecular weight. These steps are represented in Equation 5 for a 1,4- addition to butadiene. A somewhat similar set of formulas could be written for a 1,2-process.



(5)

Isoprene undergoes similar changes[9] but with greater ease in the metalation step which can occur after phase 1.

This metalation was judged[9] to occur because the carboxyl groups in the dimeric fraction exceeded the number needed for this stage of chain growth. Its likelihood was shown by the metalation of compounds[10] which had structures similar to units that would be present in a 1,4-polybutadiene rubber, as illustrated with numerous olefins (Table II) and their even more numerous products. Dotted vertical lines emphasize similarities between the unit and models. Metalation occurred in each case and very easily in diallyl, which is most like the 1,4-polybutadiene. Hence, polymerization by addition converts the monomer to a product extremely susceptible to attack by the catalyst in another way; special attention is called also to the many shifts of double bonds, a further example in the multiple but orderly changes. The consequences to alfin polymerization or to any sodium polymerization are obvious.

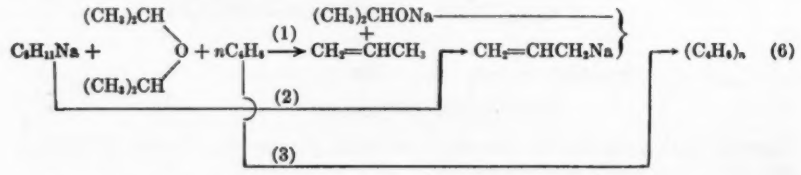
A more striking example of cascading processes occurred with the discovery of the alfin catalyst[11]. Diisopropyl ether was being used as a coördinating agent for the sodium ion, somewhat after the way ordinary ether serves the Grignard reagent. A solution of the ether and diene in pentane was added

TABLE II. METALATION OF OLEFINS WITH STRUCTURES SIMILIAR TO PORTIONS OF A RUBBER

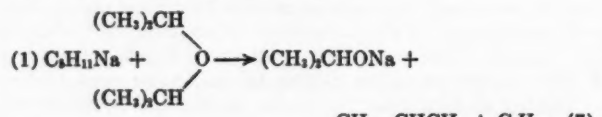
Compound	Formula	Products of Metalation by Amylsodium
Polydiene unit	$(-CH_2\|CH=C\|HCH_2\|CH_2\|CH=CH\|CH_2-)_n$	
Diallyl	$CH_2=C\|HCH_2\|CH_2\|CH=CH_2$	$CH_2=CH\bar{C}H(\overset{+}{N}a)CH_2CH=CH_2$; $Na\overset{+}{C}H-CHCH_2CH_2CH=CH_2$; $Na\overset{+}{C}H-CHCH_2CH=CHCH_3$; $Na\overset{+}{C}H-CHCH_2CH_2CH=C\bar{H}Na^+$
1-Butene	$CH_2=C\|HCH_2\|CH_3$	$CH_2=CH\bar{C}H(Na^+)CH_3$; $Na\overset{+}{C}H_2CH=CHCH_3$; $Na\overset{+}{C}H-CHCH_2CH_3$; $Na\overset{+}{C}H-CHCH_2C\bar{H}_2Na^+$
Propylene	$CH_2=C\|HCH_3$	$CH_2=CHC\bar{H}_2Na^+$; $Na\overset{+}{C}H-CHC\bar{H}_2Na^+$
Ethylene	$CH_2=C\|H_2$	$CH_2=C\bar{H}Na^+$
Isobutene	$CH_2=C(CH_3)CH_2$*	$CH_2=C(CH_3)C\bar{H}_2Na^+$; $CH_2=C(C\bar{H}_2Na^+)_2$

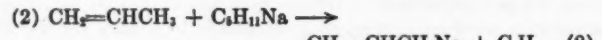
* Isobutylene is comparable to a unit in a polyisoprene.

dropwise (as for Equations 4 and 5) to amylsodium which was being vigorously stirred in pentane. Within seconds, two distinct steps were inserted before the butadiene was attacked by the organosodium reagent, and the full set of reactions yielded a band of rubber completely insoluble and nonswelling in all common solvents and which wrapped about the propeller. The multiple equation for this process is:



For clarity the separate steps are given in full.





Each step was proved by a separate reaction. Separate tests of each salt for catalytic activity were negative, but the joint action was positive. Sodium isopropoxide is as essential as allylsodium. Although seemingly a pair of unrelated ions, its connection with the activity of allylsodium is as specific as

that found in the second phase of the Wurtz reaction (Table I and Equation 3), where inorganic components were as obvious part of the reagents.

The present method[12] of preparing the catalyst no longer uses this ether. Amylsodium is prepared as usual. Alcohol is added to destroy half or more of the amylsodium, thereby furnishing the alkoxide in a finely divided state. Propylene is then passed into the mixture. These steps are shown in Equations 10, 11, and 12.

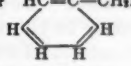
$$C_5H_{11}Cl + 2Na \rightarrow C_5H_{11}Na + NaCl \quad (10)$$

$$C_5H_{11}Na + (CH_3)_2CHOH \rightarrow (CH_3)_2CHONa + C_5H_{12} \quad (11)$$

$$C_5H_{11}Na + CH_2{=}CHCH_3 \rightarrow CH_2{=}CHCH_2Na + C_5H_{12} \quad (12)$$

All operations are carried out in the high-speed stirring apparatus[13] under an atmosphere of dry nitrogen. Half of the product is sodium chloride, which remains with the catalyst. From some preparations[14] gentle centrifuging or decanting throws out first the traces of sodium metal left by the failure of the first step to be 100 per cent, and, secondly, the small amount of blue sodium chloride that often accompanies Wurtz reactions. The remainder is the mixture of catalyst and sodium chloride that remains suspended indefinitely.

TABLE III. GENERAL AND SPECIFIC FORMULAS FOR SOME ALFIN CATALYSTS AND VISCOSITIES OF CORRESPONDING POLYBUTADIENES

Alcohol	Hydrocarbon	$[\eta]$
$RCH(CH_3)ONa$	$CH_2{=}CHCH(R)Na$ or $HC{\equiv}C{-}CH_2Na$ 	
$(CH_3)_2CHONa$	$CH_2{=}CHCH_2Na$	11–13
$nC_3H_7(CH_3)CHONa$	$CH_2{=}CHCH_2Na$	12–13
$C_6H_5(CH_3)CHONa$	$CH_2{=}CHCH_2Na$	6–7
$(CH_3)_2CHONa$	$[CH_2{\cdots}CH{\cdots}CHCH_2]Na$	6–7
$(CH_3)_2CHONa$	$C_6H_5CH_2Na$	6–7
$(CH_3)_2CHONa$	$[CH_2{=}CHCHCH_2CH{=}CH_2]Na$	11–12
$nC_3H_7(CH_3)CHONa$	$[C_2H_5CH{\cdots}CH{\cdots}CH_2]Na$	<2

Many other combinations have been tried[15]. In general, the alkoxide must come from a secondary alcohol, one branch of which is a methyl group; the olefin must have the essential system —CH=CH—CH_2—, which may be part of a ring as in toluene. A few combinations are given in Table III, together with the intrinsic viscosities attained by their use on butadiene at room temperature in about 5 volumes of pentane by common bottle polymerization technique.

In addition to these catalysts, a few pairs of salts show somewhat similar catalytic activity. For example, phenylsodium with sodium chloride[16] is a poor catalyst, and with sodium bromide is a much poorer one, capable, however, of being improved a little by addition of sodium chloride preferably prepared in situ by reaction with an alkyl chloride. Amylpotassium[16] with the potassium chloride formed during its preparation (Equation 13) has catalytic activity at −30° C, but at 0°

$$C_5H_{11}Cl + 2K \rightarrow C_5H_{11}K + KCl \quad (13)$$

acts like any ordinary reagent, that is, as in Equation 5. The polymers formed from these catalysts have low intrinsic viscosity (1 or less) and little practical interest. They, however, help clarify ideas of the phenomenon.

DISTINCTIVE FEATURES OF ALFIN CATALYSTS AND POLYMERIZATION

Alfin catalysts are different[11] from the conventional sodium compounds or sodium metal in every respect. The components are specific (see Table III). They cause polymerization in minutes, whereas the same quantity of ordinary sodium reagent requires considerably more time. The best catalyst is the fastest agent known for polymerizing butadiene. The great speed can be demonstrated in a soft-drink bottle where a few milliliters of catalyst suspension with a solution of 30 cc. of butadiene in 150 cc. of pentane will set the mass to a solid gel within seconds and make the contents erupt from the cork-stoppered bottle within about 2 minutes.

The intrinsic viscosity quickly reaches 12 and above whereas, the same amount of sodium reagent for the same time in the ordinary sodium polymerization produces a polymer much lower. No intermediate steps can be isolated, whereas in the ordinary process, mono-, di-, tri-, and other low intermediate adducts can easily be shown to be present.

A group of novel relationships centers about the velocities and viscosities[11]. For example, per equivalent quantity of reagent or catalyst, the regulation of either velocity or viscosity rests solely in the catalyst. One catalyst causes an extremely rapid polymerization to a polymer of a specific molecular weight. Another catalyst induces the reaction at a different rate to a molecule of different size. Even more striking is the fact that, in general, those catalysts which cause the fastest polymerization produce polymers with the highest intrinsic viscosity. Still more surprising is the constancy of intrinsic viscosity, irrespective of the amount of catalyst used. Isoprene can be added to a large excess of an alfin catalyst and the viscosity be the same as when the catalyst is added to isoprene. These features are not found with other polymerizing agents.

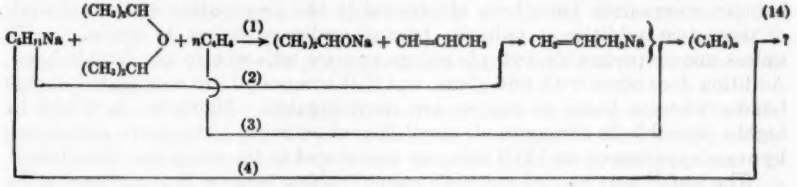
The high proportion of 1,4-addition in the alfin process contrasts with the tendency toward 1,2-addition in the ordinary sodium polymerization at room temperature. The new process resembles the present emulsion method in this one respect. x-Ray diffraction measurements[17] have also shown a regular pattern for the alfin polybutadiene. All results indicate high control of the process—more than other reagents exert.

The contrast between butadiene and styrene[18] is also unusual. With ordinary organosodium reagents, say, amylsodium, styrene polymerizes much faster than butadiene. With the alfin catalyst, butadiene polymerizes nearly five times faster. Also, the intrinsic viscosity of the alfin polybutadiene (11 to 13) is much higher than the alfin polystyrene (1.1 to 3.6, depending on the amount of sodium isopropoxide present), which in turn is higher than polystyrene[19] made by the same mole proportions of an ordinary sodium reagent. In copolymerization the styrene rate is more nearly equal[20] to the butadiene and is possibly faster[21].

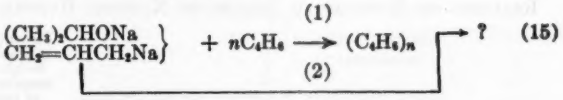
The action of ethylene dibromide and ethyl benzoate as agents to stop polymerization is different for the two classes of polymerizing agents that contain sodium ions[14]. For polymerizations induced by amylsodium or like reagents, these two compounds increase the intrinsic viscosity of the polymer, because the polymer anions, like all anions of organosodium compounds, are joined to give a product twice or more the size obtained when methanol stops polymerization. When the same reagents are used in an alfin process the intrinsic viscosity remains constant.

PROBLEMS IN THIS STUDY

Secondary or multiple reactions.—One of the major problems is the tendency of organosodium reactions to cascade to low levels of activity, shown in nearly every reaction so far examined. Hence the three-step Equation 6 that represents the discovery of the alfin catalyst should be made a four-step one (Equation 14) to provide for further action (probably metalation) of amylsodium on the polymer.



The particular problem in alfin catalysis can similarly be expressed in Equation 15 because the catalyst is still an organosodium reagent capable of reactions common to such compounds.



What, therefore, is the action of metalating agents on a polydiene, and how can we be assured that this secondary reaction is metalation rather than some other manifestation of normal activity?

Table IV lists the most common reactions—metalation, addition, cleavage, and the Wurtz—of organosodium reagents[22].

Metalation belongs to the general type of acid-salt interchange[22] typified by the reaction of sodium acetate with a halogen acid. Addition occurs between amylsodium and butadiene, but is best illustrated by the reaction with 1,1-diphenylethene[23], where the sodium ion becomes attached to the adjacent carbon and the amyl ion to the second one. Of all carbon-carbon double bonds, this

TABLE IV

COMMON REACTIONS OF ORGANOSODIUM COMPOUNDS

Metalation

$C_5H_{11}Na + HR \rightarrow C_5H_{12} + NaR$

$[CH_3CO_2Na + HX \rightarrow CH_3CO_2H + NaX]$

Addition

$C_5H_{11}Na + CH_2{=}CHCH{=}CH_2 \rightarrow CH_2{=}\underline{C}HCH(Na)CH_2C_5H_{11}$

$C_5H_{11}Na + (C_6H_5)_2C{=}CH_2 \rightarrow (C_6H_5)_2\underline{C}CH_2(Na)C_5H_{11}$

$C_6H_5Na + (C_6H_5)_2C{=}CH_2 \rightarrow$ no reaction

Cleavage

$C_5N_{11}Na + (C_2H_5)_2O \rightarrow C_2H_5ONa + C_5H_{12} + C_2H_4$

Wurtz and related type

$C_5H_{11}Na + C_5H_{17}Cl \rightarrow C_5H_{12}.C_5H_{17}$ (or $C_5H_{14} + C_5H_{16}$) $+ NaCl$

one has proved most suitable for tests. Phenylsodium[23] does not add, and this failure has a bearing on the explanation of the catalytic process. The cleavage reaction with ordinary ether is the same type that took place in the discovery of the catalyst. The process is extremely fast.

Only the first two reactions need be considered, because carbon-carbon cleavage by this class of reagents is unknown in aliphatic compounds, and all halogen compounds have been eliminated in the preparation of the catalyst. of these two, addition is unlikely, because ordinary olefins do not so react[22], unless one or preferably two phenyl groups are adjacent to the double bond. Addition does occur with butadiene, but that compound has conjugated double bonds, whereas those in rubber are unconjugated. However, it would be highly desirable to eliminate all possibility of addition or to prove metalation by some experiment, and this idea was uppermost in the series described below.

The tests[24] were carried out with natural rubber because that material is the purest type of a 1,4-polymer obtainable. Four different types of reagents were used (see Table V). The first of these, the alkoxide, never adds to carbon-carbon double bonds of any type, whether activated by adjacent phenyl groups

TABLE V

REACTION OF METALATING AGENTS ON NATURAL RUBBER

Increasing severity of reagent		Percentage range of insoluble materials with increasing severity of reagent or condition	
		Min.	Max.
1	$Na^{+}OR^{-} + HRu \rightarrow Na^{+}\bar{R}u + HOR$	4	53
2	$Na^{+}[\bar{C}H_2\cdots CH{-}CHC_2H_5] + HRu \rightarrow Na^{+}\bar{R}u + C_5H_{10}$	10	73
2	$Na^{+}C_6H_5^{-} + HRu \rightarrow Na^{+}\bar{R}u + C_6H_6$	7	80
4	$Na^{+}C_5H_{11}^{-} + HRu \rightarrow Na^{+}\bar{R}u + C_5H_{12}$	53	87

R represents an alkyl group of alkoxide.
Ru represents rubber molecule less one hydrogen used in metalation reaction.

or a part of a conjugated system. To use it as a metalating agent, the system was operated under high vacuum, so that the alcohol from any acid-salt equilibrium would be volatilized at once. Precedent for such action comes from work by McElvain[25] and coworkers on the formation of keto esters. When this agent was applied[24] under increasing severity of conditions, as attained by temperature or time variables, and with increasing activity of alkoxide, the percentage of rubber insoluble in benzene progressively increased.

The third reagent, phenylsodium, converted rubber to the insoluble product, particularly if the temperature and time of reaction were suitable, yet this reagent does not (see Table IV) add to the carbon-carbon system in diphenylethylene, the compound considered most favorable. As a metalating agent, however, phenylsodium is extremely active.

Thus two types of reagent which cannot or do not add to carbon-carbon double bonds cause the rubber to become less and less soluble; and the other two sodium compounds, which do not add to simple olefins but metalate them readily[26], also induce the same change. Especially amylsodium, the strongest metalating agent in the group, acts at room temperature and causes the largest

conversion to insoluble polymer. In general, the more severe the reagent or the condition of its use, the higher the percentage of insoluble material. Metalation is the reaction. The evidence on this point is definite.

This gel-forming reaction was proved similarly to take place with the alfin polymer; an insoluble nonswelling polymer was obtained when the alfin catalyst was discovered. There the polymer was formed in the presence of a large amount of amylsodium, an exceedingly strong metalating environment. The fourth step in that multiple reaction (Equation 4) was, therefore, extensive metalation of the product of polymerization with formation of insoluble nonswelling product.

Many chemists may be surprised that metalation causes gelling. How can cross-linking follow from a simple acid-salt interchange? With proper allowance for the cascading reactions which these sodium compounds induce, appropriate steps can be suggested. Step 2, in Figure 1, indicates one possible

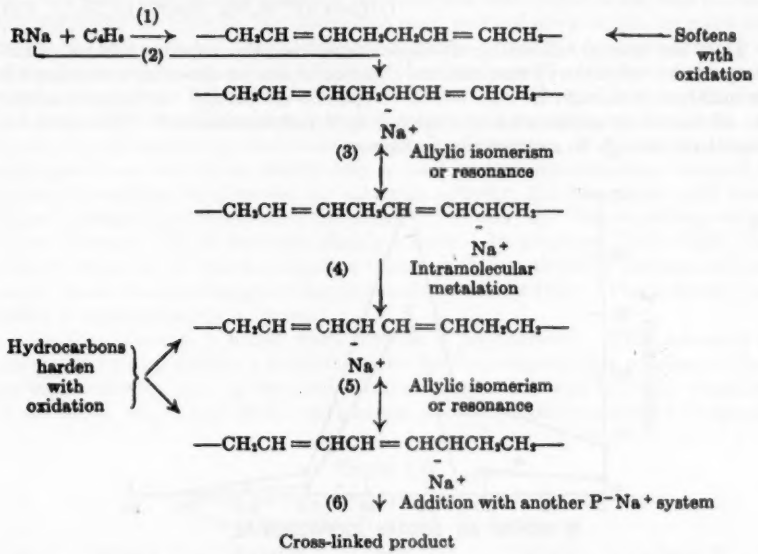


FIG. 1.—Polymerization and possible step to cross-linking by metalation. R = amyl, P = polymer.

attack by metalation. An allylic shift can then occur. An intramolecular metalation should follow, and a second allylic shift to give a conjugated diene should take place. By these steps alone a rubber that softens on exposure can change to two products which, as hydrocarbons, act as drying oils and become tough and hard by air oxidation[27]. The conjugated diene is a 1,4-substituted butadiene and, in accordance with the general properties of dienes (see Equation 4), could add any of the preceding organosodium compounds from a parallel series. Cross-linking would result. Each step in the above series is reasonable, and is known to occur with analogous compounds. Hence, the question mark at the end of Equation 4 can represent the result of several cascading reactions. A total of eight steps might have been present in the experiment when the catalyst was discovered. No guaranty can be given that this path is the only

one to the cross-linked state. For such versatile reagents, the full catalog of steps through which an initial reaction cascades to a final product will be known only after more experiments with simple compounds.

The obvious point is that the amount of catalyst should be the minimum needed for polymerization, and the conditions should be unfavorable to any secondary reaction. In short, the catalyst should tend strictly to the business of polymerization.

Effect of inorganic component.—The second major problem in this study—it stands out as clearly as the first—is the control which sodium isopropoxide exerts in the aggregate of ions that make up this catalyst. Is the quantity specific or is the organosodium compound activated for polymerization with increase of isopropoxide as if something parallel to a mass action effect could take place (Equation 16)?

$$CH_2{=}CHCH_2Na + NaOCH(CH_3)_2 \rightleftarrows CH_2{=}CHCH_2Na.NaOCH(CH_3)_2 \quad (16)$$

Does the special activating influence come from the isopropoxide ion alone? (Very recent work shows that sodium chloride is also an essential component in the catalyst, although its role is not so specific as that of the isopropoxide.) Are all reactions accelerated or changed as is polymerization? The work has progressed enough to suggest some answers.

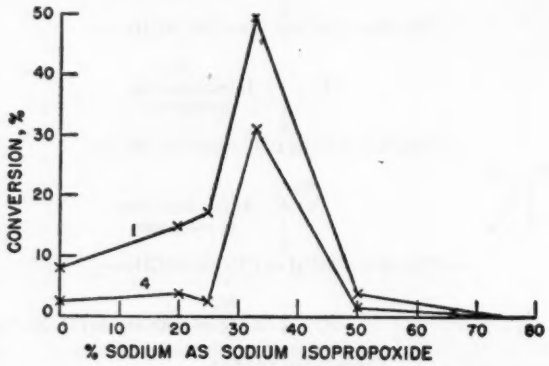


FIG. 2.—Sodium isopropoxide and catalyst activity of 1-butenylsodium.

The amounts of alkoxide needed have been studied in four cases. In three, the activity was dependent on a specific composition: sodium isopropoxide with 1-butenylsodium[28], sodium 1-phenylethodixe with allylsodium[28], and sodium isopropoxide with benzylsodium[29]. Figure 2 shows for the first pair a sharp region of maximum activity when the sodium isopropoxide content is about one-third of the catalyst components, exclusive of sodium chloride. This quantity is not an exact composition for a complex, since the metalated 1-butene[30] is a mixture of sodium compounds and the heterogeneous nature of the reagents hinders intimate contact. Nevertheless these facts indicate that the composition of the aggregate plays a part. The catalyst was actually destroyed by excess of the reagent that created it. Sometimes freshly prepared mixtures[28] had unusually high reactivity in the excess isopropoxide area, higher indeed

TABLE VI

REACTIVITY OF ALLYLSODIUM IN ABSENCE AND PRESENCE OF SODIUM ISOPROPOXIDE

Reaction with	Sodium isopropoxide, %	
	Absent	Present
Benzene	31	19
Isobutylene	38	9
1,1-Diphenylethylene	32	9
Air	Inflames	Moderately stable
Butadiene	Very slow	Extremely fast

than in the preferred region, but in the course of a month or so destruction of the catalyst always occurred. This change took place in the solid phase, because the aggregate is insoluble in pentane.

The fourth pair of ions[31], sodium isopropoxide with allylsodium, had no such specific region of activity, but seemed to form more of the complex as more isopropoxide was added. This conclusion is drawn when the separate activity of allylsodium on the left side of Equation 16 is compared[32] with that of the complex on the right. For example, Table VI shows that, in metalation, addition, or aerial oxidation, allylsodium is more active when isopropoxide is absent. It is only in polymerization that unusual activity develops, If, therefore, the ion aggregate is a mixture in which only a part of the organosodium reagent is properly combined or disposed for catalytic activity, the remainder will exert higher metalating activity than the catalyst fraction, and the percentage of gel in the polymer will be correspondingly higher. In practice (Table VII), the amount of gel in the polybutadiene is higher with low alkoxide content and becomes less as the percentage of isopropoxide increases (33). The intrinsic viscosity is approximately constant.

Another example is found when styrene is polymerized. This monomer is converted by any ordinary reactive organosodium reagent to a polymer of low intrinsic viscosity, and by the alfin catalyst to one with high intrinsic viscosity. If, therefore, only a part of the allylsodium is appropriately combined or spaced

TABLE VII

EFFECT OF SODIUM ISOPROPOXIDE ON GEL IN POLYBUTADIENE MADE BY ALLYLSODIUM

Isopropoxide[a], moles	Series[b] A			Series[b] B			Series[b] C			Series[b] D			Series[b] E		
	Y %	[η]	Gel %	Y %	[η]	Gel %	Y %	[η]	Gel %	Y %	[η]	Gel %	Y %	[η]	Gel %
10	28	11	16	—	—	—	—	—	—	—	—	—	—	—	—
12	51	14	11	—	—	—	—	—	—	—	—	—	—	—	—
16	61	16	11	—	—	—	65	12	66	25	12	29	—	—	—
20	71	—	4	86	14	28	55	15	32	24	12	21	39	15	39
24	—	—	—	83	12	23	—	—	—	—	—	—	44	12	15
26	—	—	—	—	—	—	—	—	—	43	12	19	—	—	—
26	—	—	—	87	14	15	48	12	19	—	—	—	40	11	13
32	—	—	—	32	12	8	—	—	—	2	12	6	30	12	13
34	—	—	—	54	14	12	—	—	—	—	—	—	—	—	—
36	—	—	—	—	—	—	5	10	3	—	—	—	—	—	—

[a] Moles of isopropyl alcohol for each gram equivalent of sodium metal used in making catalyst. Maximum possible amount of allylsodium was 0.50. Actual amount obtained was 0.40. Isopropoxide was made at expense of allylsodium.

[b] Five separate series were tested. In each series preparations were as nearly uniform as possible. Yield (Y), intrinsic viscosity [η], and gel were determined for each sample except one in Series A.

with the isopropoxide and this amount increases as the latter increases, the intrinsic viscosity of the polymer also increases correspondingly. In practice (Table VIII), this result, too, is realized[18].

This combination of salts, therefore, differs from the first three in its greater stability toward large amounts of alkoxide. It forms a polybutadiene higher in intrinsic viscosity (11 to 13) than those from the other three, which are in the vicinity of 7.

Catalyst composition showed its influence also when lithium isopropoxide was used to increase the concentration of isopropoxide, but not sodium ion in the aggregate. The activity was considerably lessened, and in some cases destroyed, when one mole or more of lithium isopropoxide[34] was present for each mole of catalyst. On the other hand, the activity was not destroyed when the same method was used to introduce as high as 5 additional moles of sodium isopropoxide or to introduce potassium isopropoxide. The deduction in this case is complicated by the fact that the lithium salt retards the formation of the catalyst from reaction of amylsodium with propylene, but in any event the lithium salt has a different effect from the corresponding sodium one.

TABLE VIII

EFFECT OF SODIUM ISOPROPOXIDE ON INTRINSIC VISCOSITY OF POLYSTYRENES MADE BY ALLYLSODIUM

Allylsodium	Ratio[a] alkoxide/ allyl	Time min.	Yield %	Yield[b] me.	[η]
0.68	16	30	61	90.3	3.61
1.35	16	31	103	76.3	2.47
0.92	4	30	27.9	30.2	3.09
1.4	4	30	38.4	27.8	3.15
2.3	4	30	87.4	37.8	2.78
4.1	1	30	57.5	14.1	1.77
5.5	1	30	65.0	11.9	1.62
2.2	1	30	16.9	7.7	1.84
5.55	0	31	26.5	4.8	0.78

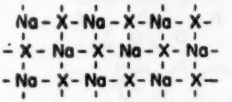
[a] Moles of sodium isoproproxide to allylsodium.
[b] % yield divided by milliequivalents of allylsodium used.

These results emphasize the control that inorganic components exert. The organosodium compound is an insoluble aggregate of ions. Its character is changed, often drastically, when its environment in the aggregate is changed. This aspect sets these reagents well apart from those which must operate in a solvent where the ions are dispersed.

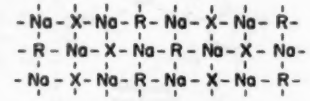
Many more problems exist in this field, but the above discussion shows how much is in common with ordinary chemical reactions. The overall alfin process is regarded as a series of chemical reactions, and the object is to limit it to polymerization, as the more easily controlled Wurtz reaction eventually was stopped at the end of its first phase. Efficient use of catalyst and improved composition are means to that end. Until this goal is attained, little work on the chemical properties of the polymer is in order, for the polymer must be considered an impure mixture until secondary reactions have been eliminated. In other words, the necessary purification that should precede all work on organic compounds must, in this case, come by purification of the reaction itself. In large measure, therefore, the catalyst is responsible for everything—initiation, termination, and points between.

NATURE OF THE REACTION

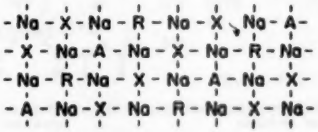
The unique properties of the alfin reagent naturally raise the question of how it operates. No precise answer can yet be given, but the known physical and chemical properties of organosodium salts suggest how a compound may act in more than one way. First of all, the reagents are insoluble aggregates of ions, in part like sodium chloride, because half of each aggreate is composed of that salt.



SODIUM CHLORIDE



AMYLSODIUM R = C_5H_{11}



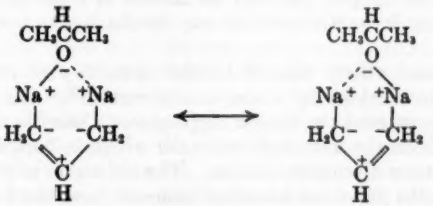
AN ALFIN CATALYST

A = ALKOXYL R = ALKENYL

Coördination valencies bind the aggregate together. In sodium chloride the coördination number[35] of sodium is 6, and the crystal has been called a giant molecule or polymer[36]. Therefore in the alfin aggregate a coöordination valence of 4 or 6 is reasonable. In such environment the sodium ions of the isopropoxide and allyl salts can have equivalent activity through either a linear or cyclic arrangement that might happen to exist on, or in, a portion of the aggregate. Simultaneously the allyl ion is bound firmly at each end. In either structure the sodium ion is not attached solely to a particular anion. The volume of the ions would affect coördination. Only a fraction of the ions might pack together properly to give the specific structures needed for catalytic activity.

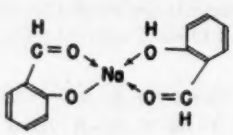
Linear structure (A = alkoxide ion)

Cyclic structure

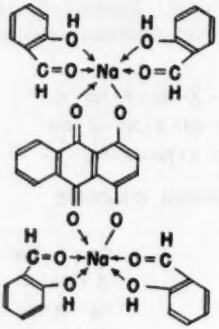


Coördination between sodium and organic ions need not be considered unusual. It must occur in all these reagents to render them insoluble. Furthermore, coördination compounds have for some time been known to occur be-

tween organic compounds and sodium salts that have appropriate structures. Sidgwick[37] and others precipitated a number of these, whose analyses corresponded with coördination values of 4 and 6. Chemical reactions also indicated the existence of such systems.



Quadri-covalent



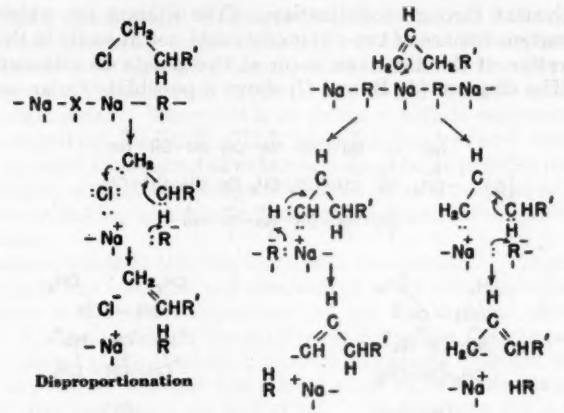
Coordination compounds of sodium

Sexi-covalent

All reactions with reactive organosodium salts can occur on the surface of the aggregate, from which no pair of ions, much less a single one, need escape to react in solution. This idea is supported by three facts: The medium, pentane, is the poorest solvent known for ionic compounds, no solution of the reagent has ever been detected, and the amount of polymer approximately doubles and triples as the catalyst is proportionately increased[28], whereas no increase should have resulted in a solution already saturated by the reagent.

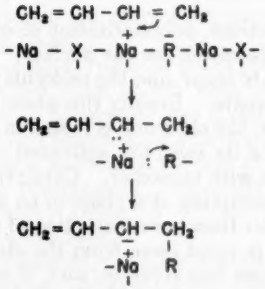
Reactions clearly depend on more than the anion or the organosodium salt. A single alkoxide, sodium isopropoxide, accelerates metalation by amylsodium, retards metalation or addition reaction by allylsodium, drastically alters the polymerization induced by allylsodium, and at first alters and then destroys the polymerization induced by butenylsodium. The related lithium isopropoxide reduces or destroys the unique polymerization created by the presence of sodium isopropoxide on allylsodium, although potassium isopropoxide does not. These changes and numerous others are too diverse to be accounted for by the assumption that the alkoxide is merely an inert surface over which the organosodium reagent is dispersed and made more available. They indicate an actual control of the reaction of an organosodium reagent by another specific ion or salt. The possibilities of control by change of the ion environment in such aggregates are unique, yet fully as diverse as those found in the conventional type of organic reactions which rely on changes in temperature, solvent, pH, etc.

These facts and others related to the chemistry of organosodium compounds can be provided for by a simple explanation[38]. All processes begin by adsorption of the reagent on the ion aggregate. Coördination takes place by aid of electrons from the adsorbed molecule, which in turn is activated and in part at least becomes a potential anion. The old anion is thus gradually freed for reaction with the polarized adsorbed molecule, and the final product results by a few simple electron shifts. This series of changes, illustrated for disproportionation in the Wurtz reaction and for metalation of an olefin, accords nicely with current concepts of valence[35] and the attractive influence[38] of cation for anion.



Manner of reaction with ionic aggregate

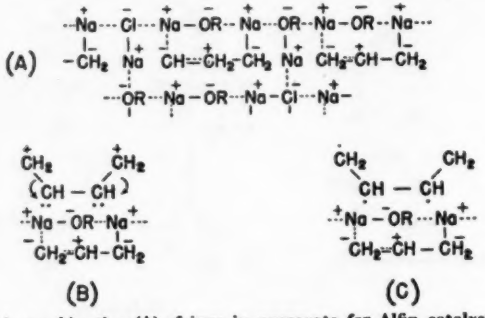
As applied to the ordinary or sodium process of polymerizing butadiene, adsorption and activation occur as usual and the old anion adds with simple electron shifts to give a new anion. The process is repeated over and over to give a large polymer. A definite salt is formed at every step. The process can be called compound polymerization. At all times the growing polymer is an anion.



For alfin polymerization and the two other fast ones that occur with phenylsodium and amylpotassium, a new factor enters. The anion has reduced reactivity of the ordinary kind, that is, for the concluding phase of the addition reaction. Allylsodium[32] adds to 1,1-diphenylethylene at a reduced rate, phenylsodium[23] does not add at all (see Table IV), and amylpotassium[16] shows its catalytic activity at a low temperature, where the normal addition reaction should be retarded. Hence, the adsorbed monomer has a longer period in the activated state. Opportunity is thus provided for reactions with another monomer, possibly similarly activated, instead of the old anion. The process can escape from the vicinity of the anion and become catalytic and can continue at least as long as the old anion remains embedded in the ionic aggregate (the stability factor), or until some specific size is attained.

The sodium isopropoxide may help in some way other than by anchoring the organic anion. The sodium ions of the alkoxide and allylsodium might

become equivalent through coördination. (The lithium ion which normally has a coördination valence of two obviously could not fit easily in this scheme.) Hence adsorption of the diene can occur at two points simultaneously rather than one. The diagram (A, B, and C) shows a possibliity for an assumed ag-



Possible combination (A) of ions in aggregate for Alfin catalyst and adsorption of diene to give a pair of carbonium (B) or free radical (C) centers

gregate that contains all the ions known to be present. Polar bonds (solid lines between ions) and coördinate bonds (dotted lines) obviously are interchangeable. It shows also electron shifts in the adsorbed diene, so as to produce either a pair of carbonium or free radical centers. In either case a type of polymerization, radically different from the ordinary sodium one, would result.

In summary, all reactions, polymerization or otherwise, with organosodium compounds start by adsorption on the surface. Activation of the adsorbed reagent is then assumed to occur, and the molecule is ripe for a reaction in which the old anion can participate. Usually this phase passes smoothly to form the new anion. If, however, the old anion is rooted in the ion aggregate or is otherwise unable to complete its role, the activated molecule can follow another course, namely, reaction with monomer. Catalytic polymerization is, thereby, a consequence of an interruption at a phase of an ordinary reaction.

This picture is simpler than the assumption of an active anion center which in some unknown way is pried loose from the strongly polar influence of the sodium cation and escapes into solution; and, if such an improbable thing did occur, the anion should then undergo the familiar isomerism or show resonance as it grows, so that the polymer would be largely a 1,2-product, and chain termination would be random. In general, the idea of separate and sole anion activity is contrary to the common behavior of organosodium reagents, which are, after all, highly subject to control by inorganic components in the reagents and, as in the case of alfin catalysts, to remarkable control by seemingly unrelated salts. No fact yet found and no speculation on the reaction encourage the idea that the alfin process involves a free anion at any stage of growth or is lacking in the exceedingly high degree of control found, by diligent search, in other organosodium reactions.

PROGRESS TOWARD PRACTICAL USE

The difficulties in the practical use of the interesting alfin polymer lie in its toughness. The polybutadiene does not soften on the mill as does natural

rubber. This result might be charged to its very high intrinsic viscosity or perhaps more accurately to the secondary reactions. Attempts to obtain one of lower viscosity by regulating polymerization in any of the conventional ways are unsuccessful because such catalysts act slowly and the product becomes highly contaminated. The result is an ordinary sodium polymerization, not to mention secondary reactions. This situation has reduced this end of the problem to one of eliminating all side reactions as far as possible from the fastest acting catalyst, so that the product is as pure an alfin polymer as possible, free from the cross-linking and double bond rearrangements that are the aftermath of metalation.

The achievements in this way have been considerable. The polymer, when first obtained, was insoluble and nonswelling in all common solvents. Hours of extraction in a Soxhlet apparatus had not the slightest effect. By close attention to the quantity of the catalyst and freedom from organosodium reagent not related to the catalyst, a product was finally obtained which was free from gel and had an intrinsic viscosity of 11 or 13, on a few occasions even as high as 19 with less than 5 per cent of gel. Freedom from gel is, however, not enough. Possibly there were enough rearrangements of double bonds to cause structural changes that did not reach the cross-linked state (see Figure 1). At any rate, the milled product for long had the appearance of seersucker cloth, a rough uneven material with hard nodules.

Of late more improvements in the catalyst have been made and the polymerization temperature has been lowered in the hope of reducing further the secondary reactions that accompany polymerization. By this means rubbers of high intrinsic viscosity (11 to 13) have been obtained which Taft's group at the Government Laboratory at Akron has been able to mill to plastic sheets on a small tight mill through which not more than twenty-five passes are made. Obviously, progress is being made.

An approach has also been made from the use of the copolymer with styrene, which in general can be milled more readily than the polydiene. With the 80/20 copolymer the Goodyear Laboratory was able to obtain enough material for a tire test[39]. D'Ianni[39] also reported unusually good abrasion resistance in the 100 per cent polybutadiene, in spite of the lack of good milling characteristics. Taft's group[20] at the Government Laboratory at Akron has recently obtained copolymers with tensile strengths of above 4000 lbs. per sq. in. and elongations of 500 per cent and above.

x-Ray diffraction measurements made by the Goodyear[40] and Firestone[39] laboratories on an alfin polymer show a regular growth pattern. The Firestone laboratory has also noted that the distribution curve is over a very narrow range that begins with a molecular weight of 1,500,000 and extends to 2,000,000 and possibly above. These results are gratifying, but they are not measurements on the purest type of polymer possible.

Naturally, such a novel and unusually fast process has numerous problems. Many years were required to solve the problems present in the interruption of the Wurtz reaction. The experience gained in that work is helpful, but the obstacles to successful interruption in polymerization are possibly greater. Nevertheless real progress is being made.

SUMMARY

Alfin catalysts are special combinations of sodium salts which cause the rapid catalytic polymerization of butadiene to polymers of unusually high molecular

weight. These polymerizations show characteristics which are common to all reactions of organosodium compounds, namely, the tendency to undergo multiple reactions. The reagents are also insoluble aggregates of ions whose behavior is affected by the ions in the aggregate. The history of the discovery is reviewed. The catalytic polymerization shows no property in common with the conventional sodium process for polymerizing butadiene. The present problems center in the elimination of secondary reactions that are known to occur. The theory by which all the reactions occur, including polymerizations induced by organosodium compounds, is discussed. Progress toward the practical use of the alfin polymers is being made.

ACKNOWLEDGMENT

The author is greatly indebted to a large number of students who have helped materially in getting a proper background for this work as well as in making the particular experiments with the catalyst. Their names may be found in the references cited. Without their splendid coöperation the work would have been impossible.

He is also indebted to industrial laboratories for their interest and attention. The Firestone laboratories have made several measurements of the physical properties. The Goodyear laboratory has coöperated extensively in making the polymer and testing its properties for tires. The government laboratory at Akron has been a material help. It has evaluated for processibility over two hundred samples of rubber prepared in the author's laboratory in the course of efforts to improve the catalyst or its use. Without this great help a polymer which could be milled to a smooth plastic sheet could not have been obtained.

The work is supported by the Office of Rubber Reserve, Reconstruction Finance Corporation. The interest and help of its officials and staff are gratefully acknowledged.

REFERENCES

[1] Morton and Hechenbleikner, *J. Am. Chem. Soc.* **58**, 1697 (1936); Morton and Richardson, *J. Am. Chem. Soc.* **62**, 123 (1940); Morton, Davidson, and Newey, *J. Am. Chem. Soc.* **64**, 2240 (1942).
[2] Morton and Knott, *Ind. Eng. Chem. Anal. Ed.* **13**, 649 (1941); Morton, Darling, and Davidson, *Ind. Eng. Chem. Anal. Ed.* **14**, 734 (1942); Morton and Redman, *Ind. Eng. Chem.* **40**, 1190 (1948).
[3] Morton, and Fallwell *J. Am. Chem. Soc.* **60**, 1429 (1938).
[4] Morton, Davidson and Hakan, *J. Am. Chem. Soc.* **64**, 2242 (1942).
[5] Whitmore and Zook, *J. Am. Chem. Soc.* **64**, 1783 (1942).
[6] Morton, Patterson, Donovan, and Little, *J. Am. Chem. Soc.* **68**, 93 (1946).
[7] Ziegler and Baehr, *Ber.* **61**, 253 (1928); Ziegler, Croessmann, Kleiner, and Schaefer, *Ann.* **473**, 1 (1929); Ziegler, Dersch and Wollthan, *Ann.* **511**, 13 (1934); Ziegler and Jacob, *Ann.* **511**, 45 (1934); Ziegler, Jacob, Wollthan, and Wenz, *Ann.* **511**, 64 (1934).
[8] Morton and Brown, *J. Am. Chem. Soc.* **69**, 160 (1947); Morton, Brown, and Magat, *J. Am. Chem. Soc.* **69**, 161 (1947).
[9] Morton, Brown, and Magat, *J. Am. Chem. Soc.* **69**, 161 (1937).
[10] Morton, Brown, Holden, Letsinger and Magat, *J. Am. Chem. Soc.* **67**, 2224 (1945); Morton and Brown, *J. Am. Chem. Soc.* **69**, 160 (1947); Morton, Brown, and Magat, *J. Am. Chem. Soc.* **69**, 161 (1947); Morton, Marsh, Coombs, Lyons, Penner, Ramsden, Baker, Little, and Letsinger, *J. Am. Chem. Soc.*, in press.
[11] Morton, Magat, and Letsinger, *J. Am. Chem. Soc.* **69**, 950 (1947).
[12] Morton, Welcher, Collins, Penner, and Coombs, *J. Am. Chem. Soc.* **71**, 481 (1949); Morton and Little, *J. Am. Chem. Soc.* **71**, 487 (1949); Morton, Marsh, Coombs, Lyons, Penner, Ramsden, Baker, Little, and Letsinger, *J. Am. Chem. Soc.*, in press.
[13] Morton and Redman, *Ind. Eng. Chem.* **40**, 1190 (1948).
[14] Morton, A. A., and Coombs, R. S., unpublished research.
[15] Morton, Magat, and Letsinger, *J. Am. Chem. Soc.* **69**, 850 (1947); Morton and Little, *J. Am. Chem. Soc.* **71**, 487 (1949); Morton, Marsh, Coombs, Lyons, Penner, Ramsden, Baker, Little, and Letsinger, *J. Am. Chem. Soc.*, in press.
[16] Morton and Letsinger, *J. Am. Chem. Soc.* **69**, 172 (1947).
[17] D'Ianni, Naples and Field, *Ind. Eng. Chem.* **42**, 95 (1950), Dunbrook, R. F., private communication.
[18] Morton, A. A., and Grovenstein, E., unpublished research.
[19] Brady and Badger, *J. Chem. Soc.* **1932**, p. 952.
[20] Taft, W. K., private communication.
[21] D'Ianni, Naples, and Field, *Ind. Eng. Chem.* **42**, 95 (1950).
[22] Morton, *Chem. Revs.* **35**, 1 (1944); *J. Am. Chem. Soc.* **69**, 969 (1947).

[23] Morton and Wohlers, *J. Am. Chem. Soc.* **69**, 167 (1947).
[24] Morton and Ramsden, *J. Am. Chem. Soc.* **70**, 3132 (1948).
[25] McElwain, *J. Am. Chem. Soc.* **51**, 3124 (1929); Briese and McElwain, *J. Am. Chem. Soc.*, **55**, 1697 (1933); Roberts and McElwain, *J. Am. Chem. Soc.* **59**, 2007 (1937).
[26] Morton, Marsh, Coombs, Lyons, Penner, Ramsden, Baker, Little, and Letsinger, *J. Am. Chem. Soc.*, in press.
[27] Farmer, *Trans. Faraday Soc.* **42**, 228 (1946); *J. Soc. Chem. Ind.* **66**, 86 (1947); RUBBER CHEM. & TECHNOL. **20**, 366 (1947); **21**, 27 (1948).
[28] Morton, Welcher, Collins, Penner, and Coombs, *J. Am. Chem. Soc.* **71**, 841 (1949).
[29] Morton and Little, *J. Am. Chem. Soc.* **71**, 487 (1949).
[30] Morton and Holden, *J. Am. Chem. Soc.* **69**, 1675 (1947); Morton, Marsh, Coombs, Lyons, Penner, Ramsden, Baker, Little, and Letsinger, *J. Am. Chem. Soc.*, in press.
[31] Morton, Magat, and Letsinger, *J. Am. Chem. Soc.* **69**, 950 (1947); Morton, A. A., and Coombs, R. S., unpublished research.
[32] Morton and Holden, *J. Am. Chem. Soc.* **69**, 1675 (1947).
[33] Morton, Welcher, Collins, Penner, and Coombs, *J. Am. Chem. Soc.* **71**, 481 (1949); Morton, A. A., and Coombs, R. S., unpublished research.
[34] Morton, A. A., Collins, F. W., and Cluff, E. F., unpublished research.
[35] Pauling, "Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, N. Y., **1944**; Palmer, "Valency," Cambridge Univ. Press, London, **1945**.
[36] Pauling, "Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, N. Y., **1944**; Van Arkel, "Molecules and Crystals," translated by Swallow, Interscience Publishers, New York, **1949**, p. 46.
[37] Sidgwick and Brewer, *J. Chem. Soc.* **127**, 2379 (1925); Sidgwick and Plant, *J. Chem. Soc.* **127**, 209 (1925); Brady and Badger, *J. Chem. Soc.* **1932**, p. 952.
[38] Fajans, "Chemical Forces," McGraw-Hill Book Co., New York, **1931**; Morton, *Chem. Revs.* **35**, 1 (1944); *J. Am. Chem. Soc.* **69**, 969 (1947).
[39] D'Inani, Naples, and Field, *Ind. Eng. Chem.* **42**, 95 (1950).
[40] Dunbrook, R. F., private communication.

THEORY ON THE CRYSTALLIZATION AND MELTING OF UNVULCANIZED RUBBER *

I. CRYSTALLIZATION

RYOICHI KIKUCHI

PHYSICS DEPARTMENT, FACULTY OF SCIENCE, UNIVERSITY OF TOKYO, JAPAN

INTRODUCTION

Recently Wood and Bekkedahl[1] have reported new experimental results on the crystallization and melting of unvulcanized rubber in the unstretched state at different temperatures. Their results are summarized as follows:

(1). When a specimen of vulcanized amorphous rubber is kept at a constant temperature between about $+15°$ and $-50°$ C, it begins to crystallize and its volume gradually decreases, as seen in Figure 1[2]. We shall denote the ordinate, "Decrease in volume (in per cent)" of Figure 1 by $w(t)$, which is a function of time t for a constant temperature.

(2). The arrows in Figure 1 indicate the estimated values for half the total decrease of volume at each temperature. Wood and Bekkedahl considered the reciprocal of this time to be a measure of the average rate of crystallization during the first half of the volume decrease, and it is plotted against temperature in Figure 2. We should like to call this time briefly the *half-time*, and denote it by $t_{\frac{1}{2}}$.

(3). As the temperature of crystallized rubber is gradually raised, its volume increases suddenly in some region of temperature, and eventually reaches the value corresponding to amorphous state as shown in Figure 3. This phenomenon seems to be the melting of the crystal, but peculiarly the location and the width of this melting-region varies according to the previous crystallization temperature.

(4). The range of melting does not depend on the extent of crystallization and is definitely determined by the temperature at which crystallization occurs. Figure 4 is derived from Figure 3 and shows the relation between the melting range and the temperature of crystallization.

In the present paper the author tries to explain these results theoretically and consistently, with certain reasonable assumptions.

MODELS AND DEFINITIONS

Adopting the concept of the micelle (das ausgefranste Micell[3]) as a fundamental model of the rubber crystal, we may derive the following definitions.

A part of a chain molecule of rubber which works as a unit in the case of Brownian motion or crystallization is called an *element*.

When l elements in each g chain molecule arrange themselves in parallel lines, with the atomic configurations corresponding to crystalline state, this aggregation is called an *l-grain* and l is called the *size* of the grain (Figure 5).

* Reprinted from the *Journal of the Physical Society of Japan*, Vol. 4, No. 1, pages 1–10, January–February, 1949.

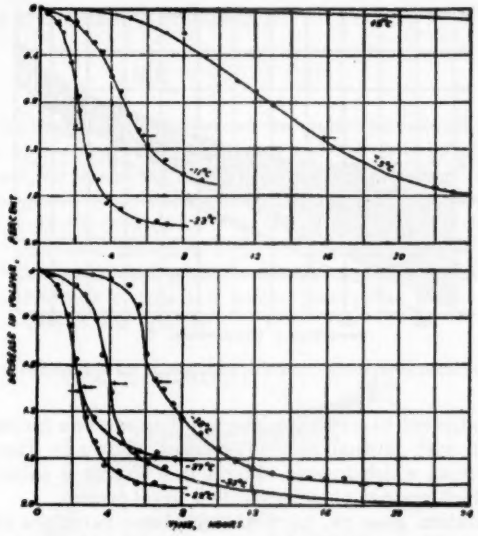


FIG. 1.—Crystallization of rubber at different temperatures, as indicated by decrease in volume.

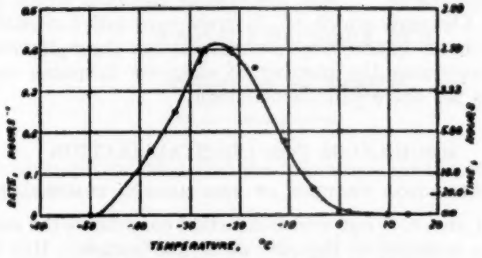


FIG. 2.—Rate of crystallization of rubber.

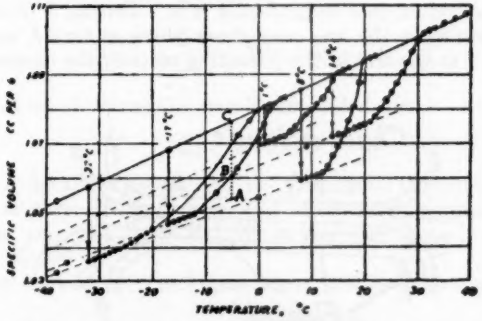


FIG. 3.—Crystallization of rubber at different temperatures and subsequent melting. (Concerning the marks A, B, and C, refer to the section on "The Melting Curve Averaged over Clusters of Various Sizes," in Part II.)

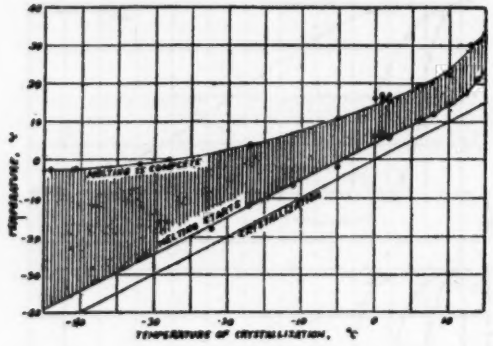


FIG. 4.—Melting range of crystalline rubber as a function of the temperature of crystallization.

At a place adjacent to a stable grain, another new one springs up. A group of grains grown with mutual connections as is shown in Figure 6 is called a *cluster*. The grains which formed earliest in a cluster is called a *nucleus*, and those grains which are not nuclei are called *usual* grains.

As crystallization goes on, narrow amorphous parts are left between two adjacent grains. Their motions being restricted by the surroudings, elements in these amorphous parts do not crystallize afterwards[4], and might be called *frozen amorphous elements*. Those amorphous elements which are not frozen are called *free*. Elements which are in grains are called *crystallized elements*. We put the ratio between the *frozen* amorphous and the *crystallized* elements as $(\gamma - 1)$: 1, γ indicating the number of elements dropping out of the free amorphous phase per one crystallized element.

MECHANISM FOR CRYSTALLIZATION

CRYSTALLIZATION PROCESS AT THE HIGHER TEMPERATURES

As mentioned above, Wood and Bekkedahl considered the reciprocal of the half-time to be a measure of the rate of crystallization. But before talking about the rate, the mechanism of crystallization must be scrutinized[5].

Let us consider that an amorphous phase containing L elements is held at T_c°K, and crystallization goes on gradually in it. Letting $P(t)$ be the number of elements remaining in the free amorphous phase at time t, and considering the definition of γ at the end of the preceding section, the number of elements

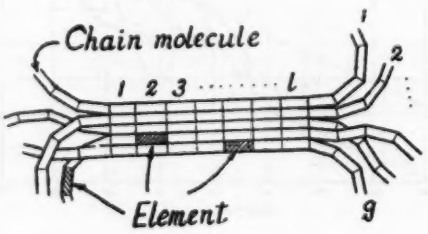


FIG. 5.—l-grain.

$Q(t)$ then having crystallized is expressed as:

$$Q(t) = \frac{1}{\gamma}\{L - P(t)\} \tag{3.1}$$

Concerning the crystallization process, we make the following assumptions. (1) The number of nuclei growing between t and $t + dt$ is $uP(t)dt$ where coefficient u depends only on the crystallizing temperature T_c but not on t. (2) From a nucleus a cluster grows linearly to right and left, as in Figure 6. and the number of newly shaped grains in time dt for a cluster is $2cdt$, where c depends only on T_c but not on t. A cluster shown in Figure 6 will be called a *linear cluster* (see Figure 8). (3) The size of each grain is equal in average, and is l_a, depending on T_c. (4) The densities in free and frozen amorphous states are equal and are different from that in the grain.

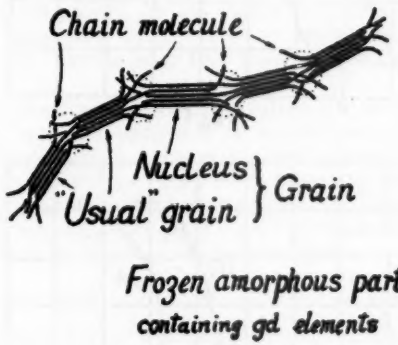


FIG. 6.—Linear cluster.

From these assumptions we derive the following equation for the number of crystallized elements[8]:

$$\frac{1}{\gamma}\{L - P(t)\} = gl_a \int_0^t 2cd\xi \int_0^\xi uP(\tau)d\tau \tag{3.2}$$

the solution of which is readily transformed into:

$$Q(t) = \frac{L}{\gamma}\{1 - \cos(\sqrt{2cugl_a\gamma}t)\} \tag{3.3}$$

which again, for small values of t, can be expanded as:

$$Q(t) \doteqdot cugl_aLt^2 \tag{3.4}$$

If, instead of the above assumption (2), we assume that a cluster grows two-dimensionally or three-dimensionally, $Q(t)$ becomes proportional to t^3 or to t^4, respectively, as long as t is small. Which of these cases is realized can be determined by Figure 1.

The relation between $w(t)$ in Figure 1 and $Q(t)$ is easily shown to be:

$$w(t) = 100\frac{v_a - v_c}{v_a} \cdot \frac{Q(t)}{L} \tag{3.5}$$

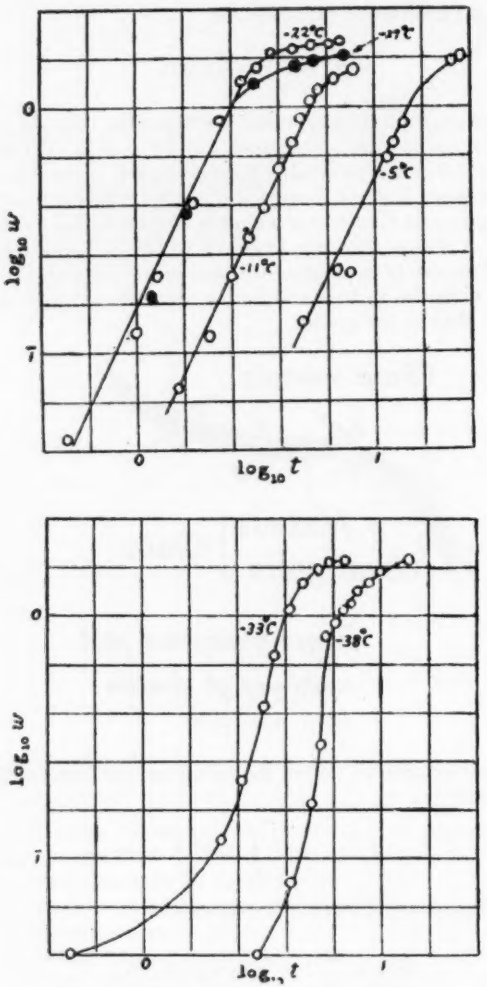


FIG. 7.—Log w *vs.* log t curves derived from Figure 1.

where v_a and v_c denote the specific volume of amorphous and crystalline states, respectively.

Figure 7 represents log w *vs.* log t curves corresponding to Figure 1. From these curves we can conclude that, for temperatures higher than about $-30°$ C, $w(t)$ is proportional to t^2 and (3.4) is realized. (3.4) might be called the *t^2-law for crystallization.*

When t is equal to the half-time t_h, we obtain from (3.4) and (3.5):

$$w(t_h) = 100\frac{v_a - v_c}{v_a} cug l_a \gamma t_h^2 \tag{3.6}$$

Combining this formula with the equation which is nothing but the definition of w (t_h) in Figure 1:

$$w(t_h) = 100\frac{1}{2}\cdot\frac{v_a - v_c}{\gamma v_a} \tag{3.7}$$

we have:

$$\frac{1}{t_h} = \sqrt{2cugl_a\gamma} \tag{3.8}$$

which is what Figure 2 represents. Substituting (3.8) into (3.4), we have:

$$Q(t) = \frac{L}{2\gamma}\left(\frac{1}{t_h}\right)^2 t^2 \tag{3.9}$$

Therefore we can conclude that, as far as γ is assumed to be independent of temperature, $1/t_h$ really is a measure of the rate of crystallization, as Wood and Bekkedahl rightly considered, for the higher temperature region. By higher temperatures we mean the temperatures at which the t^2-law holds, that is, higher than $-30°$ C. At the same time lower temperatures mean those below $-30°$ C.

However, (3.3) does not hold for large values of t, since it does not take into consideration the mutual interference of neighboring clusters. It should be added here that, by taking into account this interference in an appropriate form, we can construct a differential equation to determine $P(t)$ as a generalization of (3.2), the solution of which fits well with experimental points for large values of t, too. But to introduce too many variable parameters is futile, so the details of comparison with Figure 1 are omitted here.

CRYSTALLIZATION PROCESS AT THE LOWER TEMPERATURES

As we see in Figure 7 the t^2-law cannot explain the crystallization curves for $-33°$ C and $-38°$ C, and some other mechanisms for them should be considered. Now we assume, in place of the assumption (2) above, that a cluster grows in a shape of a tree as illustrated in Figure 8. We shall call the cluster

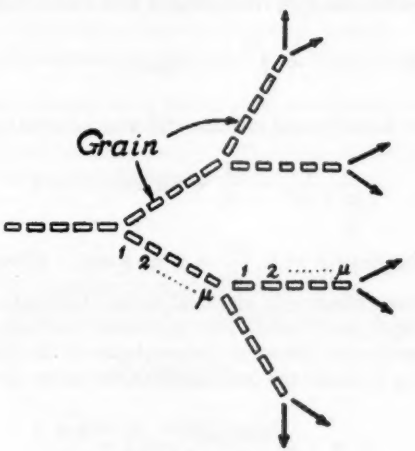


FIG. 8.—Dendriform cluster.

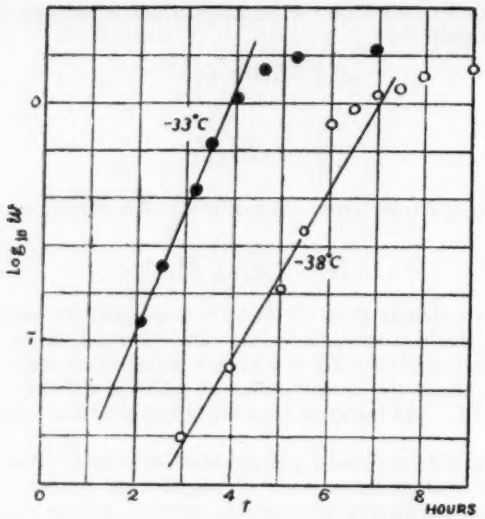


FIG. 9.—Log w *vs.* t curves derived from Figure 1.

of this form the *dendriform cluster*. If c represents, just as c in (3.2), the velocity for a grain to grow at a place adjacent to one already formed, the total number of grains included in a cluster grown from a nucleus generated at $t = 0$, is:

$$2gl_a(\mu + 2\mu + 2^2\mu + \ldots + 2^{[(ct/\mu)-1]}\mu) = 2gl_a\mu(2^{[(ct/\mu)-1]} - 1) \quad (4.1)$$

where μ has the meaning illustrated in Figure 8.

Modifying the method already described a little, we get the next equation for the number of elements $P(t)$ remaining in free amorphous phase[6]:

$$\frac{1}{\gamma}\{L - P(t)\} = \int_0^t uP(\tau)2gl_a\mu(2^{[c(t-\tau)/\mu]} - 1)d\tau \quad (4.2)$$

which can easily be transformed into the differential equation:

$$\frac{\mu}{c \ln 2}\frac{d^2P}{dt^2} - \frac{dP}{dt} + 2gl_a\mu u\gamma \cdot P = 0 \quad (4.3)$$

with the initial conditions $P = L$, $\frac{dP}{dt} = 0$ at $t = 0$. When μ approaches to infinity, (4.3) becomes effectively identical to the differential equation derived from (3.2), with slight modification in a numerical coefficient, confirming that the linear cluster can be considered as a special case of the dendriform one. On the contrary, when μ is small, the peculiarity of the latter becomes evident, and if we put:

$$\alpha^2 \equiv 1 - \frac{4\mu ugl_a\gamma}{b}, \text{ and } b \equiv \frac{c \ln 2}{2\mu} \quad (4.4)$$

the solution of (4.3) becomes:

$$P(t) = Le^{bt}\left\{\cosh(\alpha bt) - \frac{1}{\alpha}\sinh(\alpha bt)\right\} \tag{4.5}$$

And again, putting $\frac{1}{\alpha} \equiv 1 + \epsilon$, and combining (4.5) with (3.5), when ϵ is small and t is not so small, we get:

$$w(t) \doteqdot 100\frac{v_a - v_e}{\gamma v_a}\frac{\epsilon}{2}e^{2bt} \tag{4.6}$$

To check this equation, Figure 9 was drawn from the data of Figure 1 with log w and t as axes, and it shows that the exponential law (4.6) is realized for the curves of the lower temperatures. In this region Figure 2 cannot be said, in a strict sense, to represent the rate, for combining (4.6) with (3.6) we get:

$$\frac{1}{t_h} = \frac{c \ln 2}{-\mu \ln \epsilon} \tag{4.7}$$

which cannot be connected directly with b, which is the parameter representing the rate in (4.6).

RATE OF CRYSTALLIZATION

MODELS AND DEFINITIONS IN MORE DETAIL

Before we proceed further, we shall assume in more detail the process of crystallization and the properties of grains as follows.

(1) In the amorphous phase, chain molecules can assume various different forms for the same energy content, and have entropy due to the number of possible configurations. We denote this entropy S per element, and put the internal energy for this phase as zero.

(2) In the first step of the formation of an l-grain, and l-activated complex is formed, with the shape shown in Figure 10. Elements in the activated complex have value zero for both entropy and internal energy.

(3) An element in a grain has the value $-E$ for internal energy and zero entropy.

(4) A grain does not exist alone but appears and disappears together with a frozen amorphous part composed of $g\delta$ elements, each of which has the values zero of both entropy and internal energy. The value of δ is, as shown in Figure 6, $2d$ for a nucleus and d for other usual grains.

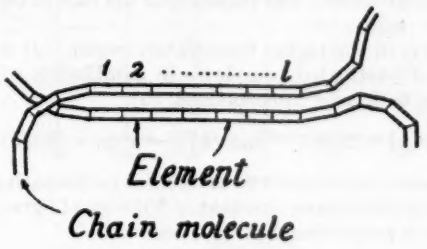


FIG. 10.—l-activated complex.

When we want to emphasize the presence of the frozen amorphous part, we write such as l-δ-grain. The existence of this part is important because it exerts influence on the crystallization energy of a grain, the latter having meaning only for a system containing both the grain and the frozen amorphous part belonging to it, as they both appear and disappear at the same time. Therefore the crystallization energy per element of an l-δ-grain is $-El/(l + \delta)$.

(5) In both amorphous and crystalline states, thermal motion (chiefly vibration) is assumed nearly equal and the difference of volumes in the two states multiplied by the atmospheric pressure small compared with ST or E. Hence the free energy per element (chemical potential) for each state is as follows:

$$\left.\begin{array}{ll} \phi_{am} = -ST & \text{for amorphous state} \\ \phi_{ac} = 0 & \text{for activated complex} \\ \phi_{lb} = -El/(l + \delta) & \text{for } l\text{-}\delta\text{-grain} \end{array}\right\} \tag{5.1}$$

(6) The temperature defined by equating ϕ_{am} and ϕ_{lb}:

$$T_m = \frac{E}{S}\frac{l}{l + \delta} \tag{5.2}$$

will be called the *characteristic melting point* for an l-δ-grain, as the latter melts at temperatures higher than T_m. Introducing T_0, defined by $E = ST_0$, the formula for the size $l(T, \delta)$ of a grain of melting point $T°$ K is:

$$l(T, \delta) = \delta\frac{T}{T_0 - T} \tag{5.3}$$

T_0 gives the melting point of a grain for which $l/\delta \rightarrow \infty$.

RATE OF FORMATION OF A GRAIN

For the process of formation of a grain from the amorphous state through the activated complex, so far as the rate of transfer from the latter to the final crystal is fast enough, the rate-determining factors are the following: (1) the rate of diffusion of elements in the course of formation of an activated complex from the amorphous phase, and (2) the number of activated complexes in equilibrium with the amorphous phase, when the diffusion velocity is sufficiently large.

In the lower region of temperature (1) has the chief effect, and both u and c are proportional to $\exp(-U/kT)$, where U is the activation energy for diffusion of an element. Though the details are not described here, this assumption serves to explain qualitatively the variation of the rate of crystallization in the lower temperature region.

On the contrary, in the higher temperature region, (2) is rate-determining, and the number of l-activated complexes in equilibrium with the amorphous phase is, according to Eyring[7], proportional to:

$$\exp\{-2l(\phi_{ac} - \phi_{am})/kT\} = \exp(-2lS/k) \tag{6.1}$$

where 2 in the power represents two molecules participating in the activated complex and k is the Boltzmann constant. Number of l-grains, $r(l, T)$, crystallizing in unit time is proportional to (6.1) and

$$r(l, T) = A \exp(-2lS/k) \tag{6.2}$$

At a temperature T, grains smaller than $l(T, \delta)$ of (5.5) are unable to crystallize, and the total number of grains formed in unit time $r_\delta(T)$ is:

$$r_\delta(T) = \int_{l(T,\delta)}^{\infty} r(l, T)dl = A\frac{k}{2S}\exp\{-2l(T, \delta)S/k\} \tag{6.3}$$

The rate of formation of a grain, u and c, are proportional to (6.3).

The total number of elements $P_d(T)$ crystallizing in usual grains in unit time is:

$$P_d(T) = \int_{l(T,d)}^{\infty} gl r(l, T)dl \tag{6.4}$$

and, therefore, the average number of elements gl_a for a usual grain is:

$$gl_a = \langle gl\rangle_{Av} = \frac{P_d(T)}{r_d(T)} = g\frac{k}{2S}\left\{1 + 2l(T, d)\frac{S}{k}\right\} \tag{6.5}$$

COMPARISON WITH EXPERIMENTS

For the higher temperature region, the theoretical results of the former section can be compared with Figure 2, which represents (3.9). Supposing the number of nuclei is much smaller than that of usual grains, we get, from (6.3), (6.5), (5.3) etc.:

$$\begin{aligned}\frac{1}{t_h} &= \sqrt{2cugl_a\gamma} \\ &= B\left(1 + 2q\frac{T}{T_0 - T}\right)^{\frac{1}{2}}\exp\left(-3q\frac{T}{T_0 - T}\right)\end{aligned} \tag{7.1}$$

where B is a function containing γ, etc., but is considered simply as a constant for preliminary comparison with experiments, and q stands for Sd/k.

In Figure 11, points and the broken curve are those of Figure 2, and the

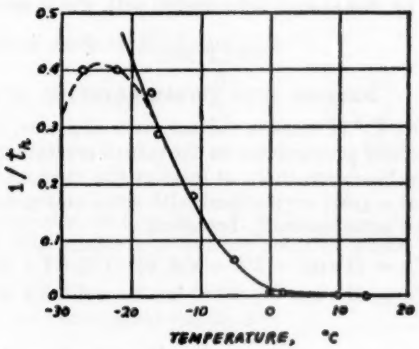


FIG. 11.

○ Experiment

——— Theory

solid line is the theoretical result (7.1) with the values:

$$\begin{aligned} T_0 &= 310^\circ \text{ K} \qquad B = 500 \\ q &= 0.5\text{–}0.005\ (T\text{-}273) \end{aligned} \tag{7.2}$$

which were selected so as to get the best fit with experimental results, and the probable error of T_0 is about $\pm 20°$.

Though the formula (7.1) and the values of (7.2) have merely an approximate meaning, the satisfactory agreement shown in Figure 11 indicates that such a theory is plausible. Especially as mentioned at the end of the section on "Models and Definitions," T_0 being the upper limit of the existence of any crystal of rubber, $T_0 = 310°$ K means that, however long it may be held at a constant temperature, rubber cannot crystallize above 37° C. Though in reality, some evidences of rubber crystals near 50° C were reported[1], the value of (7.3), with its probable error, does not seem irrational, when the possibility of variation of this threshold value with the change in previous thermal treatments or in compositions of the rubber sample is considered.

This theory will be concluded in Part II of this investigation[8].

REFERENCES

[1] Wood and Bekkedahl, *J. Applied Physics* **17**, 362 (1946); RUBBER CHEM. & TECHNOL. **19**, 1145 (1946).
[2] Figures 1, 2, 3 and 4 are duplications of the corresponding figures of Wood and Bekkedahl (reference No. 1) except for the designations A, B, and C in Figure 3, which will be explained in Part II of this investigation (the following paper in this issue of RUBBER CHEMISTRY AND TECHNOLOGY).
[3] Abits, Gerngross and Hermanns, *Naturwissenschaften* **34**, 754 (1940) and subsequent papers.
[4] Parks, *J. Chem. Physics* **4**, 459 (1936); Treloar, *Trans. Faraday Soc.* **37**, 81 (1941).
[5] Von Gölera and Sachs, *Z. Physik* **77**, 281 (1932); Avrami, *J. Chem. Physics* **7**, 1103 (1939); **8**, 212 (1940); **9**, 177 (1941).
[6] Strictly speaking, the number of elements crystallized as nuclei, $u_0 l_\infty \int_0^t P(\tau)d\tau$, should be added on the right-hand side of (3.2) and (4.2), but physically it is assumed to be negligible when compared with the rest of the terms, as long as t is small.
[7] Glasstone, Laidler, and Eyring, "The Theory of Rate Processes," New York, 1941, p. 185.
[8] Part II is the paper following this one in this issue of RUBBER CHEMISTRY AND TECHNOLOGY.

II. MELTING

In this paper it will be attempted to explain the melting properties of rubber crystals discovered by Wood and Bekkedahl[1], with the same notations and definitions as in Part I.

MELTING

MELTING OF A LINEAR CRYSTAL

Clusters grown at $T_c°$ K contain various sizes of grains, but their distribution $n_0(l, T_c)$ is definitely proportional to the rate of crystallization as a function of l, that is, $r(l, T_c)$, Equation (6.2), at least at the moment of crystallization. Now we assume that a grain crystallized with size l enlarges to $l + \lambda$ in time[2], the distribution for l asymptotically becoming:

$$\left.\begin{aligned} n(l, T_c) &= D \exp\{-2(l-\lambda)S/k\} \quad l \geqq l(T_c) + \lambda \\ n(l, T_c) &= 0 \qquad\qquad\qquad\qquad\quad l < l(T_c) + \lambda \end{aligned}\right\} \tag{8.1}$$

(see Figure 12).

In the next place, we assume that the melting of a linear crystal takes place by the following mechanisms: (1) melting proceeds step by step from both ends of a cluster; and (2) a grain with the characteristic melting point $T°$ K does not melt until the temperature becomes higher than $T°$ K.

For example, when we raise the temperature of a cluster crystallized at T_c° K to T° K, melting proceeds from both ends step by step until a grain with its characteristic melting point T'° K ($T' > T$) becomes located at the edge of the cluster, and then the melting stops there. Until the temperature becomes higher than T'° K, melting does not resume.

EVALUATION OF THE PROBABILITY

As a preliminary we must solve the next question on probability: "One card marked 'R' the number of which is R and one card marked 'W' the number of which is W, are placed upside-down at random at each of the M sites in a line, M being equal to $R + W$. Turning the cards one by one from both ends and continuing so far as the mark 'R' appears, what is the average number of cards that is to be turned?"

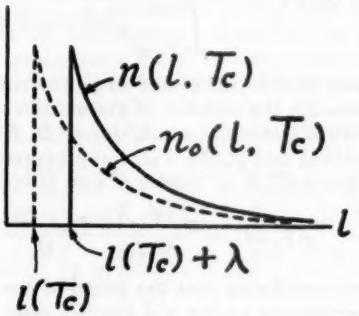


FIG. 12.

The probability $\Psi(s)$ of finding an 'R' at the s-th site from an end, after all the $(s-1)$ th have been 'R', being:

$$\Psi(s) = \frac{R}{M} \cdot \frac{R-1}{M-1} \cdots \frac{R-s+1}{M-s+1} \,. \tag{9.1}$$

the average number of cards $m(M, R)$ asked is:

$$m(M, R) = 2\langle s \rangle_{M} = 2 \sum_{s=1}^{R} \Psi(s) = \frac{2R}{M-R+1} \qquad \text{for } R \leqq M-1 \tag{9.2a}$$

$$m(M, R) = R \qquad \text{for } R \geqq M-1 \tag{9.2b}$$

It is important because at $R = M - 1$, $m(M, R)$ is an angled curve as a function of R, and this results in a distinct point at which melting ceases, as will be shown later.

Though, strictly speaking, (9.2a) holds for only integral values of R, we assume its validity for nonintegral values, too.

MELTING OF A CLUSTER

Suppose that a cluster formed at T_c° K and of size M (when grains contained in a cluster are M in number, we shall call its size M), is brought to T° K

($T > T_c$). Then from (8.1) the number of grains R having the characteristic melting point below $T°$ K is given by:

$$R = \int_{l(T_c)}^{l(T)} n(l, T_c)dl = D\frac{k}{2S}\{e^{-2l(T_c)(S/k)} - e^{-2(l(T)-\lambda)(S/k)}\} \tag{10.1}$$

and M is equal to $R(T = T_0)$:

$$M = \int_{l(T_c)}^{\infty} n(l, T_c)dl = D\frac{k}{2S}e^{-2l(T_c)(S/k)}. \tag{10.2}$$

In a cluster crystallized at $T_c°$ K, the average size of a grain which has melted at $T°$ K, $gl_a(T_c, T)$ is:

$$gl_a(T_c, T) = \frac{\int_{l(T_c)+\lambda}^{l(T)} gle^{-2(l-\lambda)(S/k)}dl}{\int_{l(T_c)+\lambda}^{l(T)} e^{-2(l-\lambda)(S/k)}dl} \tag{10.3}$$

Considering R and M thus calculated to be the corresponding quantity in (9.2), $m(M, R)$ represents the number of grains which have melted at $T°$ K. Then, to compare with experiments, combining $m(M, R)$ with (10.3) and $gl_a(T_c)$ in (6.5), which is nothing but $gl_a(T_c, T_0)$, the proportion $y(T, M)$ of elements which have melted below $T°$ K in cluster of size M becomes:

$$y(T, M) = \frac{gl_a(T_c, T)}{gl_a(T_c)} \cdot \frac{m(M, R)}{M} \tag{10.4}$$

In the next place considering that the width of the frozen amorphous part left between two neighboring grains is d directly after the crystallization and becomes gradually $d - \lambda$, $l(T_c)$ and $l(T)$ has the form:

$$l(T_c) = d\frac{T_c}{T_0 - T_c}, \quad l(T) = (d - \lambda)\frac{T}{T_0 - T} \tag{10.5}$$

Then if we define T_b by:

$$(d - \lambda)\frac{T_b}{T_0 - T_b} = d\frac{T_c}{T_0 - T_c} + \lambda \tag{10.6}$$

it gives the temperature at which melting begins, because at $T = T_b$, we obtain easily $R = 0$ from (10.5) and (10.1).

Using T_b, (10.4) becomes:

$$y(T, M)\begin{cases} = \dfrac{2}{M \cdot x(T) + 1} Y(T) \equiv y_1(T, M) & T \leqq T_m' \quad (10.7a) \\ = Y(T) \equiv y_2(T, M) & T \geqq T_m' \quad (10.7b) \end{cases}$$

where:

$$Y(T) = 1 - \frac{1 + 2q\left(1 - \dfrac{\lambda}{d}\right)\dfrac{T}{T_0 - T}}{1 + 2q\left(1 - \dfrac{\lambda}{d}\right)\dfrac{T_b}{T_0 - T_b}} \cdot x(T) \tag{10.8}$$

$$x(T) = \exp\left\{-2q\left(1 - \frac{\lambda}{d}\right)\left(\frac{T}{T_0 - T} - \frac{T_b}{T_0 - T_b}\right)\right\} \tag{10.9}$$

and T_m' is determined by the equation:

$$M \cdot x(T_m') = 1 \tag{10.10}$$

It should be mentioned here that, at $T = T_m'$, $R = M - 1$ and T_m' gives the point at which melting apparently ends for the cluster.

THE MELTING CURVE AVERAGED OVER CLUSTERS OF VARIOUS SIZES

From our standpoint we can interpret the ratio $\overline{AB}/\overline{AC}$ in Figure 3 of Part I to be the proportion of the number of elements which have melted at $-5°$ C to the total number of cyrstallized elements at $-17°$ C. To compare this quantity with our theory, we have to average $y(T, M)$ over M, because $y(T, M)$ is concerned only with clusters of size M, and rubber crystallized at any temperature contains clusters of various different sizes.

To proceed along this line, the distribution of the number of clusters with size M must be determined in advance. Though this distribution should be derived theoretically from assumptions concerning the procedure of crystallization, so far as the preliminary theory is concerned we can do with the next assumption[3]: "the number of clusters with sizes between M and $M + dM$ is constant, *i.e.*, is independent of M."

Then averaging $y(T, M)$ of (10.7) over M, we obtain:

$$\begin{aligned} z(T) &\equiv \langle y(T, M) \rangle_{Av} \\ &= \frac{1}{M_m} \left\{ \int_{1/x(T)}^{M_m} y_1(T, M) dM + \int_0^{1/x(T)} y_2(T, M) dM \right\} \\ &= \frac{Y(T)}{M_m \cdot x(T)} \left[2 \ln \left\{ \frac{M_m x(T) + 1}{2} \right\} + 1 \right] \quad \text{for } T \leqq T_m \end{aligned} \tag{11.1a}$$

$$z(T) = \frac{1}{M_m} \int_0^{M_m} y_2(M) dM = Y(T) \qquad \text{for } T \geqq T_m \tag{11.1b}$$

where T_m is determined by the equation:

$$M_m \cdot x(T_m) = 1 \tag{11.2}$$

and M_m gives the maximum size of clusters crystallized at $T_c°$ K, being of the order[4]:

$$M_m \approx \left(\frac{c}{ugl_a\gamma} \right)^{\frac{1}{4}} \tag{11.3}$$

It should be noted here concerning (11.1), that $z(T)$ changes its functional form and undergoes a remarkable change of tangent at T_m just as $y(T, M)$ at T_m', and is, for T greater than T_m:

$$1 > z(T) \gtrsim 1 - \frac{1}{M_m}, \text{ for } T > T_m \tag{11.4}$$

Therefore, T_m can be considered to be the point at which melting apparently ends.

The formula (11.1) can be compared with the experiment with appropriate values of parameters. Figures 13 and 14 give this comparison, with the values of T_θ and q given in (7.2) and with

$$\begin{aligned} T_b - T_c &= 5° \text{ (below } 10° \text{ C)} \\ M_m &= 40 \text{ at } T_c = 1° \text{ C} \end{aligned} \tag{11.5}$$

M_m having the functional form (11.4).

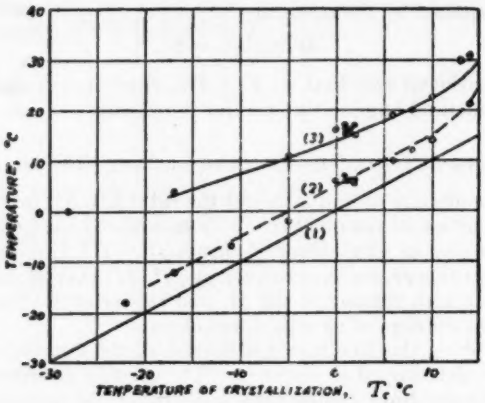


FIG. 13.—(1) Temperature of crystallization T_s. (2) Assigned values of T_s. (3) Theoretical values of T_m by (11.2). ○ Experimental points.

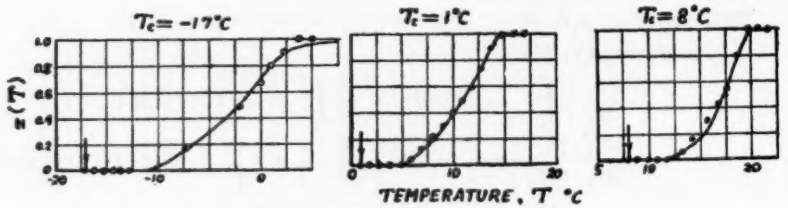


FIG. 14.—○ Experiment ——— Theory.

These figures indicate that (11.1) agrees well enough with the experiment as far as the linear crystal is concerned, except in the region over about 10° C. This discrepancy above 10° C is not explained yet.

DISCUSSION AND CONCLUSION

Melting of the dendriform clusters.—For this crystalline form, two theoretical curves for melting could be constructed by assuming laws for the process of melting, but conclusions cannot yet be drawn because of the complexity of the formulas. Qualitatively, the reason for the broadening of the temperature range of melting at the lower temperatures seems to be due to the larger values of the size of a cluster M_m as the temperature becomes lower.

Recrystallization.—When rubber is held at a constant temperature half-way to the melting point or above the temperature at which melting has apparently finished, the rubber begins to decrease in volume gradually. Wood and Bekkedahl called this phenomenon recrystallization, the peculiarity of which is that the rate of decrease in volume is larger than for primary crystallization. This phenomenon is explained without difficulty for our theory. Namely, not to speak of the case in which the melting is apparently not completed, in the case, too, in which the rubber is brought to a temperature higher than that at which the melting has apparently ended, the crystal does not melt completely and at least some quantity of the order of (11.5) is left, which plays the role of nuclei

for recrystallization, with resultant larger rate of decrease in volume. Though this seems very interesting and important for more thorough investigation, more experimental data are desirable.

Furthermore, other experimental results, too, reported by Wood and Bekkedahl, *e.g.*, various facts concerning stark rubber, can be explained at least qualitatively by our models.

In conclusion, we should like to point out that the present theory includes some new bold models concerning the micelle of high polymers. Though in the present stage these models are nothing but hypotheses, we hope that in the near future their validity will be examined experimentally by attacks from various sides.

ACKNOWLEDGMENT

The author wishes to express his cordial thanks to Professor T. Sakai, the late Mr. Y. Ochi, and Messrs. A. Ishihara and H. Ichimura for their encouraging discussions.

REFERENCES

[1] Wood and Bekkedahl, *J. Applied Physics* **17**, 362 (1946); RUBBER CHEM. & TECHNOL. **19**, 1145 (1946).

[2] The author feels that this assumption is less serious than the following two. The former was introduced to distinguish the point at which melting begins (see Figures 3, 4, 13, and 14). Even without this assumption, the theoretical melting curves of these in Figure 14 do not change essentially, and only start smoothly from the temperature at which crystallization has occurred.

[3] This distribution of clusters is derived when the interference in growth of neighboring clusters is taken into account in such a form that the rate of growth of a cluster is proportional to $P(t)$, as defined in the section on the "Crystallization Process at the Higher Temperatures," in Part I.

[4] If, in accordance with the discussion in the section on the "Crystallization Process at the Higher Temperatures," in Part I, clusters are assumed to grow independently of one another, we can derive the result:

$$M_m = \frac{\pi}{\sqrt{2}} \left(\frac{c}{u_0 l_a \gamma} \right)^{\frac{1}{2}}$$

and if the assumption[3] that "the number of clusters with size between M and $M + dM$ is constant, *i.e.*, is independent of M", is valid, we obtain:

$$M_m = 2 \left(\frac{c}{u_0 l_a \gamma} \right)^{\frac{1}{2}}$$

STRESS-STRAIN PROPERTIES OF NATURAL RUBBER UNDER BIAXIAL STRAIN *

B. B. S. T. BOONSTRA

RUBBER FOUNDATION, DELFT, HOLLAND

INTRODUCTION

Stress-strain properties for rubber stretched in two directions have been reported by Ariano[1] and by Treloar[2].

Both authors used rectangular test-pieces, and neither of them succeeded in attaining high elongations because of the low tear resistance of rubber under biaxial stress.

High elongation was reached by the first author by inflating spherical samples; however, the strain in the majority of cases is about identical in the two directions. In this paper a system is described which allows stretching to high elongations in two directions independently of each other.

According to this method, tube-shaped samples are stretched in the direction of the tube axis and at the same time are inflated to cause tangential elongation. The axial stresss is partly measured on the dynamometer, the rest and the transverse stress are calculated from the air pressure in the tube. In this way stress-strain curves can be obtained for stresses parallel and at right angles to the tube axis as a function of the elongations in the two directions.

The theoretical equations extended to this case may then be checked. Besides, the decay of stress (axis-parallel) with time was measured and the influence of elongation perpendicular to this stress determined.

EXPERIMENTAL PROCEDURE AND RESULTS

PREPARATION OF THE SAMPLES

Glass tubes of 16–25-mm. diameter were repeatedly dipped in a latex dispersion of the following formula:

Rubber (in form of 40 per cent latex)	100	
Colloidal sulfur	2	in form of 33 per cent
Zinc oxide	2	dispersion with 0.2
Butyl Zimate	1	per cent Darvan
Latekoll (ammonium polyacrylate)	1	

After a layer of sufficient thickness was obtained (0.25–0.40 mm.), the tubes were first dried at room temperature, then for 30 minutes at 80° C, and finally were vulcanized for 15–30 minutes at 110° C in live steam or hot air.

* Reprinted from the *Journal of Applied Physics*, Vol. 21, No. 11, pages 1098–1104, November 1950. This paper is Communication No. 124 of the Rubber Foundation.

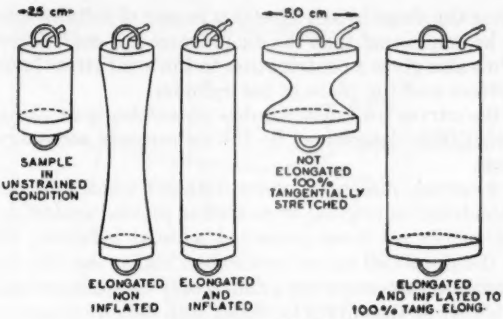


FIG. 1.—Test-samples of biaxial strain.

Dumb-bells punched out of these tubes showed the following properties:

Tensile strength	320–360 kg. per sq. cm.	
Elongation at break	750–800 per cent	
Load at 300 per cent elongation	17– 21 kg. per sq. cm.	
Hardness (Shore *A*)	38	
Elasticity (Shore *G*)	85	
Permanent set after 24 hours at 200 per cent elongation	measured after 1 hour	2.5 per cent
	measured after 24 hours	0 per cent

The rubber tubes are fastened on ribbed metal cylinders coated with a layer of vulcanized rubber (carbon black mix).

These cylinders can be attached to the dynamometer clamps; one of them has an air inlet connected to a manometer and a small hand operated air pump.

The tubes are elongated on a Schopper tensile tester (1) with air free to flow in and out; (2) inflated with air to the original diameter; (3) fastened on oversize clamp cylinders so that a constant transverse elongation can be maintained by pumping air into the tube.

The principle is illustrated in Figure 1 and some experimental values in Table I.

TABLE I

SOME EXPERIMENTAL VALUES OF TENSILE TESTS ON INFLATED TUBE-SAMPLES (SERIES 2) AT 100 PER CENT TANGENTIAL ELONGATION. STRESSES ARE CALCULATED IN KG./SQ. CM. OF THE ORIGINAL CROSS-SECTION. r = ORIGINAL RADIUS OF THE TUBE; α_z = AXIAL EXTENSION RATIO; α_t = TANGENTIAL EXTENSION RATIO; d = ORIGINAL THICKNESS OF THE WALL OF THE TUBE; p = AIR PRESSURE IN THE TUBE IN CM. HG

Average d = 0.033 cm.	Tangential elongation 100 per cent	Axial elongation in per cent							
		25	50	100	200	300	400	500	600
	I Dynamometer axial stres (kg. per sq. cm.)	0.8	1.8	5.7	10.8	17.7	27.9	46.3	111.5
	II Pressure p (cm. Hg.)	6.8	6.2	5.1	5.1	4.5	4.4	4.4	6.5
	III Axial stress (calculated from $0.0272r/dp$ kg. per sq. cm.)[a]	7.2	5.8	5.3	5.3	4.7	4.6	5.0	.69
	I+III Total axial stress (kg. per sq. cm.)	8.0	8.6	11.0	16.1	22.5	32.5	51.3	118.4
	IV Tangential stress (kg. per sq. cm.)[b]	9.3	8.7	10.7	15.9	18.8	23.0	26.7	46.9

[a] General formula: $(13.6\pi r^2\alpha_z^2/2\pi rd\ 1000)\ p$.
[b] General formula: $(13.6\alpha_z\alpha_t r/1000d)\ p$.

In calculating the stress in axis direction in case of definite transverse elongation, it has to be considered that the air pressure not only determines the tangential stress but also gives a contribution to the axial stress in form of pressure against the bottom and top plate of the cylinder.

Therefore the curves for inflated tubes do not begin at elongation zero but at a definite elongation determined by the air pressure necessary for the transverse elongation.

In Figure 2 curves, measured under different conditions, are drawn, with axial stress, calculated on original cross-section plotted against axial elongation.

The lowest curves are those measured without inflation, these practically coincide with the dumbbell curve; somewhat higher lies the curve for a tube which is not elongated sideways but inflated only to retain its original diameter. Considerably higher lie the curves for tubes with definite transverse elongations.

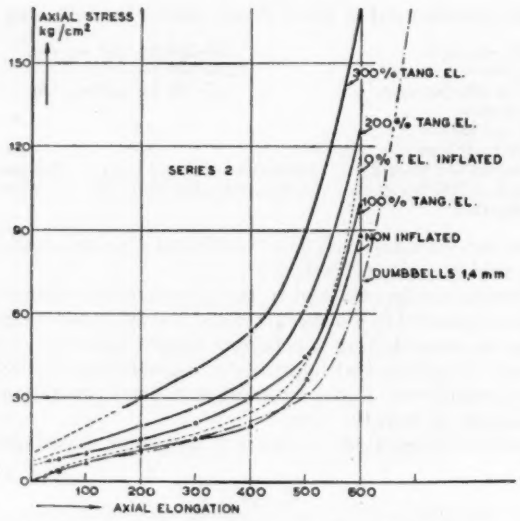


FIG. 2.—Stress-strain curves at different tangential elongations.

The pressure of the air necessary to maintain a constant diameter of the tube at the different elongations is plotted as an average of several measurements against axial elongation in Figure 3.

It will be observed in Figure 3 that the pressure drops at the highest axial elongation for the 100 per cent transverse elongation curve and also for the 300 per cent elongation curve. Probably the rubber has then become so rigid that considerable changes in pressure are possible without much effect on the diameter of the tube.

The tangential stretching force on actual cross-section is related to the pressure by the formula:

$$\sigma = \frac{13.6r\alpha_z}{1000(d/\alpha_t\alpha_z)}\, p \text{ kg. per sq. cm. on actual cross-section} \qquad (1)$$

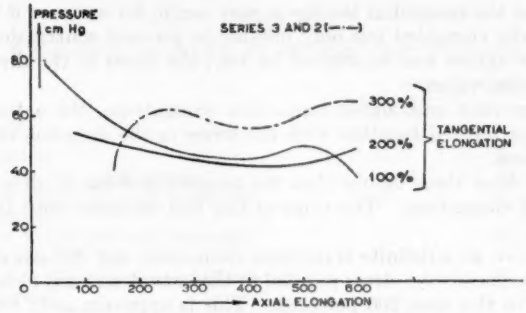


FIG. 3.—Air pressure as a function of axial elongation.

Here r = original radius of the sample, usually 12.5 mm., p = air pressure in cm. Hg, α_z = axial extension ratio, α_t = transverse extension ratio, d = thickness of wall of the tube.

So at constant pressure and the same r, the actual stress in the transverse direction is proportional to the square of the transverse elongation, (tr. el.)^2 = α_t^2, this factor is four at 100 per cent tr. el. and nine at 200 per cent.

At the same pressures the actual stress at 200 per cent tr. el. would be 9/4 of that at 100 per cent tr. el. In reality, however, the stress ratio is lower, so it can happen that the pressure at 200 per cent tr. el. is less than at 100 per cent tr. el. (Figure 3).

If the stress is plotted *vs.* the axial elongation, a set of curves is obtained as illustrated by Figure 4.

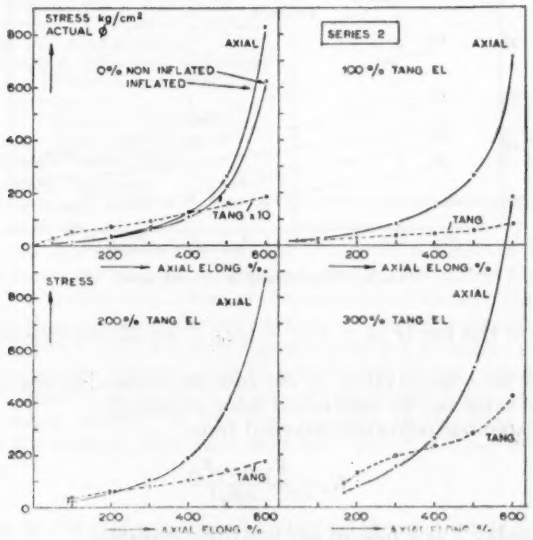


FIG. 4.—Axial and tangential stress on actual cross-section at biaxial elongation; rate of testing 30 cm. per minute.

In the case the tangential tension is very small, for instance if the sample is not tangentially elongated but only inflated to prevent contraction, the entity plotted in the figures was multiplied by ten; the stress in the direction of the axis is the actual value.

At 100 per cent and higher transverse elongations, the actual transverse stress has been plotted together with the stress in the direction of the axis, *vs.* axial elongation.

It is clear from these figures that the tangential stress in all cases increases with the axial elongation. The slope of this line increases with the transverse elongation.

Furthermore, at a definite transverse elongation, say 200 per cent, the tension must be equal to the stress parallel to the axis at an axial elongation of the same extent, in this case 200 per cent. This is approximately true; however, at 300 per cent the referred stiffness of the tube caused somewhat higher values for the transverse stress.

RELAXATION

The decay with time of the stress parallel to the tube axis was measured at the highest axial elongation, *i.e.*, 600 per cent, in the following way. The stress was measured at the moment of attaining the elongation of 600 per cent and $\frac{1}{8}$—$\frac{1}{4}$—$\frac{1}{2}$—1—2—4—8—16 and 32 minutes after that.

A linear relationship is obtained if the stress is plotted *vs.* log time, as is done for instance in Figure 5.

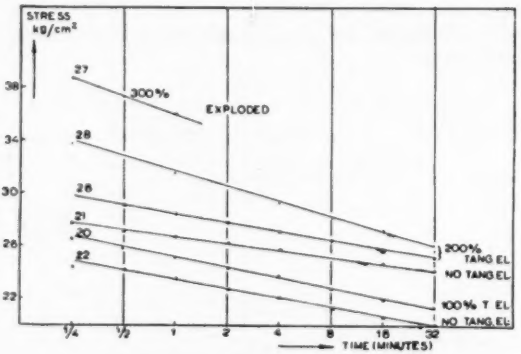


FIG. 5.—Relaxation of stress with time.

The slope of this line ($F_{1/8} - F_{32}/ - \log\frac{1}{8} + \log 32$) depends on the original stress.

Instead of the original stress, in our case the stress after one minute, F_1, is taken, as this value can be determined more accurately.

We calculated our relaxation constant from:

$$R_2 = \frac{F_{1/4} - F_{16}}{6F_1} \tag{2}$$

taking the number 2 as a base of our logarithmic system.

The relaxation constant R_2 was calculated for measurements made with tubes under variable conditions. The results are shown in Table II.

TABLE II

RELAXATION CONSTANTS AT 600 PER CENT ELONGATION

	Rate of stretching	
	15 cm./min.	30 cm./min.
Series II		
Noninflated	—	$R_2 = 0.017$
Inflated to original diameter	—	$R_2 = 0.021$
Inflated to 100 per cent tangential elongation	—	$R_2 = 0.019$
Inflated to 200 per cent tangential elongation	—	$R_2 = 0.023$
Inflated to 300 per cent tangential elongation	—	$R_2 = 0.021$
Series III		
Noninflated	—	$R_2 = 0.017$
Inflated to 100 per cent tangential elongation	$R_2 = 0.023$	$R_2 = 0.019$
Inflated to 200 per cent tangential elongation	—	$R_2 = 0.018$
Series V		
Noninflated	0.022	$R_2 = 0.018$
Inflated to original diameter	0.021	$R_2 = 0.019$
Inflated to 100 per cent tangential elongation	0.019	$R_2 = 0.020$
Inflated to 200 per cent tangential elongation	0.017	$R_2 = 0.018$
Inflated to 300 per cent tangential elongation	—	$R_2 = 0.019$
Dumbbells cut out of latex tubes	—	$R_2 = 0.017$
Dumbbells cut out of sheets vulcanized with 1.75 parts of sulfur, 20′ at 142° C in a press	—	$R_2 = 0.020$[b]
As above, but vulcanized with three parts of Tuads[a] instead of sulfur +accelerator	—	$R_2 = 0.020$[b]
As above, vulcanized with five parts of sulfur+accelerator	—	$R_2 = 0.014$
Mixture with carbon black	—	$R_2 = 0.021$

[a] Tetramethylthiuram disulphide.
[b] These vulcanisates show a value of R_2 = about 0.013 at 500 per cent axis-elongation.

It is evident from these data that the tangential elongation does not exert much influence on the relaxation constant, though the actual tension is much increased. Nor is there any influence of the nature of the mix, since soft sulfur-vulcanized rubber and thiuram-vulcanized rubber show the same relaxation constant. However, if a mix with a greater amount of sulfur, *e.g.*, five parts, is used, the relaxation constant falls to considerably lower values. This holds almost independently of the time of cure of this latter compound.

The relaxation constant is, however, sensitive to the axial elongation; at 500 per cent the value is little more than half that at 600 per cent elongation.

DISCUSSION

According to the now established statistical theory of elasticity[3] the elastic tension for unidirectional deformation is:

$$F = C[\alpha - (1/\alpha^2)] \qquad (3)$$

If one of the cross dimensions (*e.g.* the circumference of the tube) is kept constant this formula changes into

$$F_c = C[\alpha - (1/\alpha^3)] \tag{4}$$

The following simple formulation of James and Guth's theory was kindly suggested by J. Bronkhorst of the Physical Department of the Rubber Foundation.

In Figure 6, x, y, and z are dimensions of the rectangular sample. In unstrained condition $x = y = z = 1$ cm. Then total molecular stress in x, y or z direction is $C = H$ (hydrostatic pressure in unstrained condition).

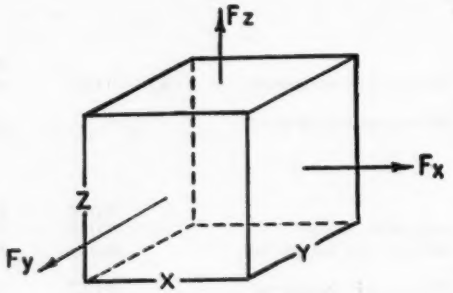


FIG. 6.—Principle of stress.

In a special strained condition x, y, z caused by forces F_x, F_y and F_z:

$F_x + Hyz = Cx$ = molecular tension
$F_y + Hxz = Cy$
$F_z + Hxy = Cz$

$x, y, z = 1$ if the volume is considered constant.

For unidirectional stress parallel to the x axis

$$F_y = F_z = 0$$
$$Cy = Hxz$$
$$Cz = Hxy$$
$$F_x = Cx - Hyz = Cx - H/x$$
$$H = Cy/xz = C/x$$
$$F_x = Cx - (C/x^2)$$

When z is kept constant by a force F_z, only $F_y = 0$ (this is not exactly true as the inflation pressure represents a small negative value which is, however, neglected),

$$F_x + Hyz = Cx$$
$$Hxz = Cy$$
$$F_z + Hxy = Cz \quad H = Cy/xz = Cy^2 = (C/x^2z^2).$$
$$F_x = Cx - Cy^2/x = C[x = (y^2/x)] = C[x - (1/z^2x^3)]$$
$$F_z = Cz - C(y^2/z) = C[z - (1/x^2z^3)]$$

Inflation to original diameter means z = constant = 1

$$F_x = C[x - (1/x^3)]$$
$$F_z = C[1 - (1/x^3)]$$

TABLE III

AXIAL STRESSES ON ORIGINAL CROSS-SECTION IN KG. PER SQ. CM.

	Axial elongation		
Series 2	50 per cent	100 per cent	200 percent
Noninflated	3.4	6.5	10.8
Inflated	4.4	7.9	12.3
Quotient	0.78	0.82	0.88
Quotient calculated from $\frac{[\alpha - (1/\alpha^2)]}{[\alpha - (1/\alpha^3)]} =$	0.87[5]	0.93[3]	0.97[5]

Inflation to 100 per cent transverse elongation ($z = 2$):

$$F_x = C[x - (1/4x^3)]$$
$$F_z = C[2 - (1/8x^2)]$$

Similarly at 200 per cent transverse elongation:

$$\left.\begin{aligned} F_x &= C[x - (1/9x^3)] \\ F_z &= C[3 - (1/27x^2)] \end{aligned}\right\}$$

At 300 per cent transverse elongation:

$$\left.\begin{aligned} F_x &= C[x - (1/16x^3)] \\ F_z &= C[4 - (1/64x^2)] \end{aligned}\right\}$$

For a definite elongation the second form is larger than the first one, so it is to be expected that the stress-strain curve for a tube inflated to original cross-section will lie at higher stresses than the curve for the noninflated tube. The difference should be relatively most pronounced at the lowest elongations.

The curves of Figure 4 are not on a convenient scale to test these relations. In Table III several data are compared.

It appears from Table III that the axial stress of the inflated tube is relatively higher than would be expected from the theoretical formula. The stress of the noninflated tubes at 100 per cent and 200 per cent corresponds to the less accurate values taken from dumbbells, which amount to 7 and 10 kg. sq. cm., respectively.

Similarly the ratio between axial stresses for noninflated tubes and tubes inflated to 100 per cent elongation is according to the theoretical derivation

$$\frac{\alpha - (1/\alpha^2)}{\alpha - (1/4\alpha^3)} \quad . \quad . \qquad (5)$$

In Table IV the calculated and experimental values are compared.

TABLE IV

CALCULATED AND EXPERIMENTAL RATIO OF AXIAL STRESS FOR NONINFLATED TUBES AND TUBES INFLATED TO 100 PER CENT TANGENTIAL ELONGATION AT VARIOUS AXIAL ELONGATIONS

Axial elongation	50 per cent	100 per cent	200 percent
Ratio calculated from.....(5)	0.74	0.89	0.97
Ratio measured in series 2	0.40	0.60	0.72
Ratio measured in series 3	0.52	0.71	0.80

Though these figures are not very accurate, they show a decided discrepancy with the calculated values; the experimental stresses being higher than those calculated.

This is even more obvious if we consider the transverse stress. Theory demands that the transverse stress, calculated on original cross-section, shall remain practically constant at axial elongations above about 100 per cent and under elongations where crystallinity disturbs the random configuration of the molecular network.

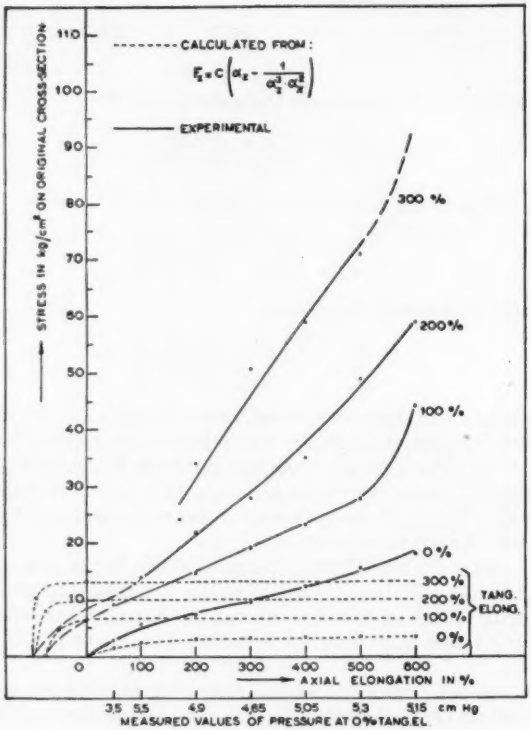


FIG. 7.—Tangential stress as a function of axial elongation.

This is illustrated in Figure 7, where the course of the tangential stress is plotted schematically for a definite value of C, *i.e.*, $C = 3.3$. This value of C can be calculated from the stress-strain curve (noninflated or dumbbell samplet as it is the axial stress where $\alpha - 1/\alpha^2 = 1$ or $\alpha =$ about 1.47 (47 per cent) elongation).

In our series 2 and 3, there is only approximate agreement at the very lowest elongations in axial or tangential direction. For instance at 0 per cent tang. el., which means that the tube is inflated only to maintain its original diameter, the calculated curve only at the very beginning is approximately followed by the experiment. At 100 per cent trans. el., however, the first point up to about 100 per cent axial elongation shows some slight agreement; at higher elongations

the difference increases strongly. It is to be expected that the constancy of volume assumed in theory will not hold exactly, but it cannot explain the wide difference between experiment and theory.

Nor is it to be expected that neglecting the small negative force in the third direction (the air pressure against the inner wall of the tube) would make much difference in the course of the theoretical curves.

So it seems that, whereas there is reasonable agreement between experiment and theory for unidirectional stress, this is no longer the case as soon as simultaneous elongation in a second direction is applied.

The high stresses above 300 per cent axial elongation may point to the fact that no equilibrium is reached; if the tube decreases a little in diameter during axial stretching and afterwards is inflated to the correct diameter, a higher pressure is necessary than when both operations are accurately synchronized.

Treloar in his experiments about two-dimensional strain plotted the force per cm. length of the extended sheet[4] (analogous to surface tension). As in his studies the strain in two dimensions was identical, the force per cm. length of the sheet is:

$$t = S_z/X^2 = F_z/X = C\left(1 - \frac{1}{X^6}\right) = C(1 - \gamma^3) \qquad (6)$$

when γ is the ratio of the final to the original thickness of the sheet and $X = Z$ the extension ratio in a direction parallel to the surface.

Treloar showed that the experimental tension force t at different extensions coincided with the theoretically derived equation:

$$t = C(1 - \gamma^4) \text{ for } C = \text{about 4 kg. per sq. cm.}$$

up to about 200 per cent elongation ($\gamma = 1/9$).

In our case the strain in the two principal directions is generally not the same, but at every tangential elongation we have one moment where axial and tangential elongation are identical. In series V we have these cases at 56, 100, 200, 275, and 300 per cent elongation. At these points of identity of the two principal strains the stresses in the two perpendicular directions must be identical too; this appears to be the case with a deviation of about the experimental error of the stress measurements.

To compare our results with those of Treloar we have plotted the force t for these cases in Figure 8, and it is evident from this figure that they agree fairly well with theoretically calculated values for $C = 5.7$ up to 200 per cent elongation. This is shown in Table V.

So far there is agreement with theory, as had been found by Treloar, except that in our case the value of C is 4.7 against 4.0 in Treloar's experiments.

This, however, may be due to the different types of mixture used.[5]

TABLE V

FORCES AT VARIOUS EQUILATERAL ELONGATIONS AND THE VALUES OF C CALCULATED FROM THESE FORCES

Elongation	Fz/X	C
56 per cent	7.9/1.56 = 5.1	5.7
100 per cent	11.2/2 = 5.6	5.6
200 per cent	17.2/3 = 5.7	5.7
275 per cent	26.5/3.75 = 7.1	7.1
300 per cent	46/4 = 11.5	11.5

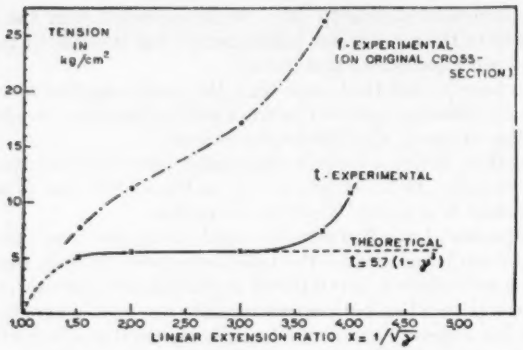


FIG. 8.—Two-dimensional equilateral extension.

In case the strains in the two perpendicular directions across the sheet are not identical, we have two principal stresses, and following again the method of plotting the entity t (stress per cm. length of the sheet), we easily derive:

$$t_x = \frac{S_x}{XZ} = \frac{F_x}{Z} = C\left(\frac{X}{Z} - \frac{1}{X^3Z^3}\right)$$

and

$$t_z = \frac{S_z}{XZ} = \frac{F_z}{X} = C\left(\frac{Z}{X} - \frac{1}{X^3Z^3}\right)$$

for $X/Z = 1$, this case simplifies again to the first problem. If we take, however, the strain situations, where X/Z is for instance $= 2$, we would expect to find a similar curve as in Figure 8 with the same value of C.

Table VI illustrates what actually is found. From Table VI it is evident that the C values do not agree with the C found for homogeneous two-dimensional strain, and differ even when calculated from the axial and tangential stress, respectively. So here also the deviations from theory are very pronounced.

TABLE VI

VALUES OF C CALCULATED FROM AXIAL AND TANGENTIAL STRESSES WITH $X/Z = 2$

Series V	Fx/Z	C calculated from Fx/Z	Fz/X	C calculated from Fz/X
Ax. el. 100 per cent Tang. el. 0 per cent	7.0– 7.5	3.7–4	2.6–3.2	6.9–8.6
Ax. el. 200 per cent Tang. el. 50 per cent	9.1	4.6	3.6	7.2
Ax. el. 300 per cent Tang. el. 100 per cent	10.1–11.8	5.1–5.9	3.9–4.0	8.0
Ax. el. 400 per cent Tang. el. 150 per cent	14.2–15.8	7.2–7.9		
Ax. el. 500 per cent Tang. el. 200 per cent	17.2–18.5	8.6–9.3	4.0–5.0	8–10

Mathematically these deviations may be accounted for partly by the treatment of Mooney[6] and more completely by that of Rivlin[7].

The formula governing the relaxation which has been used here is:

$$R = \frac{Ft_1 - Ft_2}{Ft_1/(\log t_2 - \log t_1)} \tag{7}$$

This expresses a constant decrease of stress in all time periods $t_2 - t_1$, where $t_2 = 2t_1$ and t is counted from the moment the elongation is stopped. It is an approximation of the general formula of Tobolsky and Eyring[8], and indicates that the decay of stress is the result of slippage of chain molecules along each other.

According to Flory[9], the relaxation is caused for the greater part by terminal chain slippage. This means that a rubber with longer primary molecules (before vulcanization) has a lower relaxation constant than a rubber which has been thoroughly broken down to small molecular chains on the mixing mill.

If we compare two rubbers that have undergone the same milling treatment so that we may assume about equal average molecular weight, but that have different degree of vulcanization, then the one with the highest cure shows the lower relaxation constant as the latter has the highest percentage of cross-links and relatively the lowest number of terminal chains.

This is in agreement with the observation that the vulcanizate with five parts of sulfur shows a constant $R = 0.014$, whereas the mixes vulcanized with 1.75 parts of sulfur and with thiuram only, show a value of $R = 0.020$.

At these high elongations crystallization plays a part in stress-relaxation. The crystallites begin to form at about 250–300 per cent elongation; this means that these first crystallites have a comparably low degree of orientation, lower

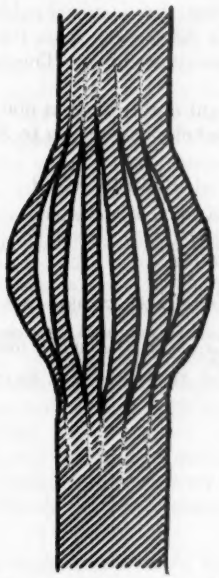


FIG. 9.—Effect of inflation on a stretched sample.

than those formed at 400–500 per cent elongation, and these again are less orientated than crystals formed at 500–600 per cent elongation.

In the latter state there are many crystallites that were in equilibrium with the surrounding amorphous mass at elongations much lower than 600 per cent.

These strive to reach an equilibrium at the now (600 per cent el.) prevailing conditions by recrystallization and detaching of terminal chains from crystallites. It is probable that such a recrystallization is a rather slow process when compared with the slippage of terminal chains, but it is difficult to distinguish between them.

Mooney, Wolstenhome, and Villars[10], besides, report indications of a relaxation mechanism of a higher rate than that found in normal analysis; its existence was established on Shore durometer readings $\frac{1}{10}$ second after stretching.

In our case, however, we would expect that transverse strain would severely hamper orientation and crystallization in axis parallel direction and diminish its contribution to stress-relaxation. The effect on crystallization can be shown experimentally by first strongly elongating one of our tube-samples and then inflating it. Very high air pressure is necessary to cause the first transverse elongation, which then does not turn out homogeneously but occurs by a definite tearing of the opaque crystallized material into streaks of thinner and clear amorphous areas and remaining crystallized fiberlike bundles. This situation is schematically drawn in Figure 9.

There has not been found any definite influence of the transverse strain on the axial relaxation. It may be that the measurements, which are technically difficult to perform and absorb much time, have not been sufficiently accurate to distinguish the differences, but then the effects could not be very pronounced.

CONCLUSIONS

(1) The stress-strain curves of vulcanized rubber held at definite tangential elongations during stretching differ more from the simple unidirectional-extension-stress curve than the theory predicts. The differences are larger at higher tangential elongations.

(2) The relaxation constant determined at 600 per cent elongation is practically unaffected by tangential elongations up to 300 per cent.

REFERENCES

[1] Ariano, *Gomma* **3**, No. 2, 31 (Mar.–April, 1939); RUBBER CHEM. & TECHNOL. **13**, 92 (1940).
[2] Treloar, *Trans. Faraday Soc.* **40**, 5 (1944); *Proc. Phys. Soc.* **60**, 135 (1948).
[3] James and Guth, *J. Applied Physics* **15**, 294 (1944); *J. Chem. Physics* **11**, 455 (1943).
[4] Treloar, *Trans. Faraday Soc.* **39**, 241 (1943).
[5] For latex rubber, Treloar mentions a value of $C = 6.3$.
[6] Mooney, *J. Applied Physics* **11**, 582 (1940).
[7] Rivlin, *Phil. Trans.* **A240**, 459, 509 (1948); **A241**, 379 (1948); **A242**, 173 (1949); *Proc. Roy. Soc.* **A195**, 463 (1949).
[8] Tobolsky and Eyring, *J. Chem. Physics* **11**, 125 (1943). The simplified formula was determined experimentally by Phillips (*Proc. Phys. Soc.* (London) **19**, 491 (1905)).
[9] Flory, *Ind. Eng. Chem.* **38**, 417 (1946).
[10] Mooney, Wolstenhome, and Villars, *J. Applied Physics* **15**, 324 (1944).

EQUIVALENT EFFECTS OF TIME AND TEMPERATURE IN THE SHEAR CREEP AND RECOVERY OF ELASTOMERS *

F. S. CONANT, G. L. HALL, AND W. JAMES LYONS

CHEMICAL AND PHYSICAL RESEARCH LABORATORIES, FIRESTONE TIRE AND RUBBER CO., AKRON, OHIO

INTRODUCTION

The dependence of creep phenomena on temperature in high polymers is well known, having been observed and discussed by a number of investigators[1]. The experiments show that, for a given time interval, the viscoelastic strain (or recovery) tends generally to rise to a higher level with an increase in the temperature of the experiment. The present series of experiments have disclosed that, for rubberlike materials, a consistent elevation of the strain-time curves with an increase in temperature is obtained, if corrections are made for the Gough-Joule effect. While a number of empirical relationships describing the dependence of viscous flow on temperature have been proposed and analyzed theoretically, no clear-cut explicit relationships have been set forth for the temperature-dependence of viscoelastic phenomena in superelastic polymers. The closest approach to such a relationship appears to be one based on a temperature function for viscosity, quoted by Leaderman[1].

The observed nature of the dependence of viscoelastic behavior on temperature implies that it should be experimentally possible to duplicate the strain S_v attained in time t_1 at temperature T_1 with an equal strain S_v attained in time t_2 at T_2. As has been indicated, a series of creep or recovery experiments on a given material, each conducted over the same time interval, but at different T, yields a family of creep (or recovery) curves; for increasing values of T the curves lie higher and higher along the S direction. From these considerations emerges the possibility of selecting a series of temperatures for these experiments such that each curve at its termini in the selected time interval matches the termini of the curves obtained at the next higher and lower temperatures. Each terminus provides the particular S_v which, given by one combination t_1 and T_1, can be duplicated by another combination t_2 and T_2. Plotted end-to-end, the curves become segments of one overall multiple-temperature curve. Tobolsky and Andrews[2] observed such a continuous relationship in analogous stress relaxation tests and proposed an implicit relationship among time, temperature, and stress. Without a knowledge of the time-temperature function, however, it does not appear possible to predict whether the general synthetic graph will be a smooth curve, without discontinuities at the junctions of the segments.

With the aim of testing the foregoing theory, as well as deriving an analytical expression for the relationship between time and temperature, observations in creep and recovery on Hevea, GR-S, Neoprene-GN, Butaprene, and Butyl rubber were undertaken.

* Reprinted from the *Journal of Applied Physics*, Vol. 21, No. 6, pages 499–504, June 1950.

APPARATUS AND METHODS

The test apparatus used has been described previously[3]. Essentially, it consists of a means of applying a shear stress to a double sandwich-type of specimen, and of observing the deformation of the specimen as the test conditions are varied. The test-specimens were also based on the same compounding formulas and cures as given in the above reference.

In the creep tests performed, the unstressed test-specimen was first brought to thermal equilibrium at the desired temperature. Twenty minutes' conditioning time was allowed after a thermocouple in the center metal web of the specimen indicated that the test temperature had been reached. A shear stress of 35.6 lb. per sq. in. was then applied quickly, and the consequent deformation noted at appropriate intervals from 5 seconds to 30 minutes after loading. In general, the measurements were made first at the lowest test temperature. After completion of the test the load was removed and the temperature of the test chamber raised. Recovery was usually found to be complete after conditioning at the next higher test temperature.

In the recovery test, the specimen was conditioned overnight (16 hours) at 35° C under load. At the end of this time, deformation had proceeded to essentially an equilibrium state. The temperature was then gradually lowered to the lowest test temperature, during which time the deformation increased because of the Gough-Joule effect. A curve of equilibrium deformation *vs.* temperature was obtained during cooling. As soon as thermal equilibrium was reached at the lowest test temperature, the load was removed and the recovery noted at appropriate intervals from 5 seconds to 30 minutes. At the end of this time the load was reapplied and the temperature raised to the next test temperature. The reestablishment of equilibrium deformation was shown by the approach of the deformation to that of the equilibrium curve previously obtained.

In a study of creep or recovery, it is often advantageous, if not necessary, to compensate for the Gough-Joule effect through a normalization of the data. Unless this is done it is found that, after a sufficient creep or recovery time, the deflection at a low temperature exceeds that at a higher temperature because of this effect. The data presented here were normalized by presenting each creep datum as a percentage of the equilibrium deformation for that temperature, and each recovery as a percentage of complete recovery.

Both creep and recovery curves were obtained on all of the stocks in the present series. The normalized data for each showed the two to be equivalent within the experimental error of either. Figure 1 shows a typical example of the close correspondence of the two types of data. Only the recovery data will be presented for the other stocks in the series.

JOINING OF RECOVERY CURVES OBTAINED AT DIFFERENT TEMPERATURES

From data such as those shown in Figure 1, it appears that the creep or recovery curves at different temperatures might be joined end-to-end to form such a continuous synthetic curve as was projected in the introduction. Such a continuous curve is meaningless, of course, unless the segments are matched so that the logarithmic time scale is continuous. Brief reflection will disclose that it is not necessary actually to procure a continuous locus of experimental points (such as could be obtained only by a fortuitous choice of temperatures) to secure a smooth multiple-temperature curve. When a series of parallel

curve segments, obtained at reasonably well-scattered temperatures and overlapping on the time scale, are available, the general continuous curve can be derived by drawing it parallel to these segments. This procedure is illustrated in Figure 2 which shows 30-minute recovery data for Hevea stock B. The data at some of the temperatures are seen to be displaced from the smooth continuous curve.

The smooth curve of Figure 2 strongly implies the existence of a continuous functional relationship between normalized creep or recovery time and temperature. Tentatively assuming its correctness, the curve may be used to supply numerical data for a set of simultaneous equations to test various t functions of T. Following this procedure, an empirical equation of the following form has been found to represent adequately the data over the entire viscoelastic region:

$$\log t_c = [C_\alpha/(T - b)] + C_\beta \qquad (1)$$

where t_c = creep or recovery time, T = absolute temperature, and C_α, b, and C_β are arbitrary constants. The resemblance of Equation (1) to the Arrhenius formula for the temperature-dependence of rate processes will be recognized.

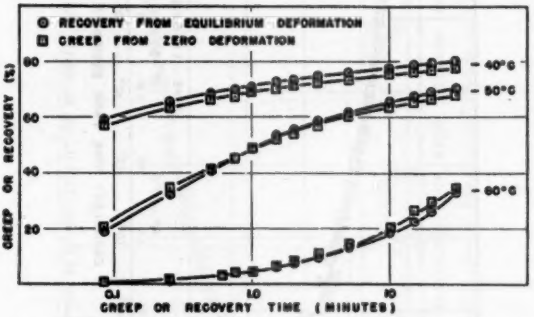


FIG. 1.—Equivalence of creep and recovery of Hevea (35.6-lb./sq. in. load).

While an estimate may be made from data such as those in Figure 2, of the temperatures at which tests should be made in order that the experimental curve segments should be on the continuous line, it is preferable, by way of testing Equation (1), to use it to derive the appropriate temperatures. Using the equation and the data in Figure 2, temperatures of −60°, −51°, −37°, −21°, +2°, and 31° C were selected for testing. Figure 3 shows that recovery curves obtained at these selected temperatures do, indeed, form a continuous multiple-temperature curve.

An additional confirmation of the equivalence of time and temperature is provided by the data in Figure 4. The experimental points show the recovery at −60° C, while the curve shows the joined recovery curves of the same specimen (Hevea stock B). The two are seen to be very nearly equivalent, for the 16-hour period of test at −60° C.

A continuous multiple temperature recovery curve for a GR-S stock is shown in Figure 5. Test temperatures were selected by an application of Equation (1) to previous data obtained at even decade temperature intervals. This curve is quite different in shape from that in Figure 3 for Hevea and reflects the more sluggish response of GR-S to low temperature stress.

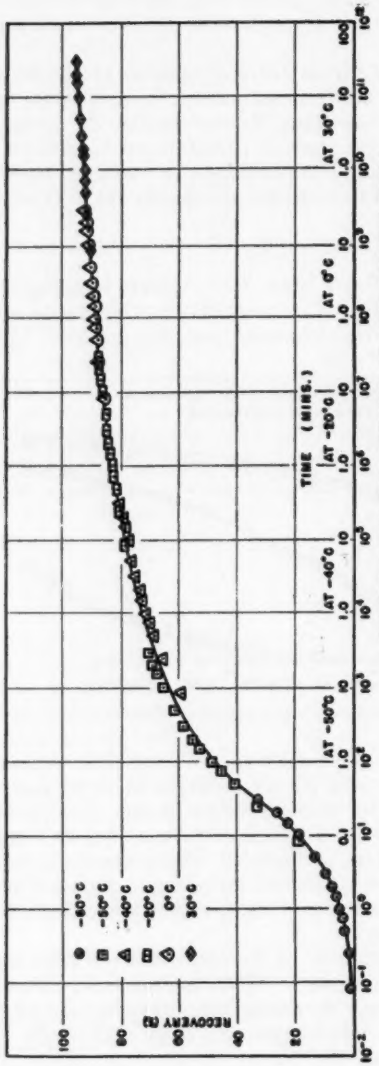


FIG. 2.—Recovery from equilibrium deformation of Hevea (35.6-lb./sq. in. load). Test temperatures taken at multiples of 10° C.

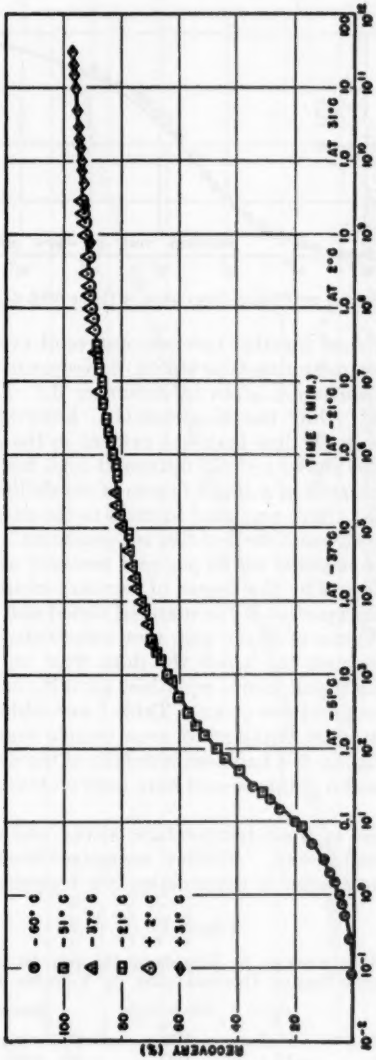


FIG. 3.—Recovery from equilibrium deformation of Hevea (35.6-lb./sq. in. load; adjusted temperature intervals).

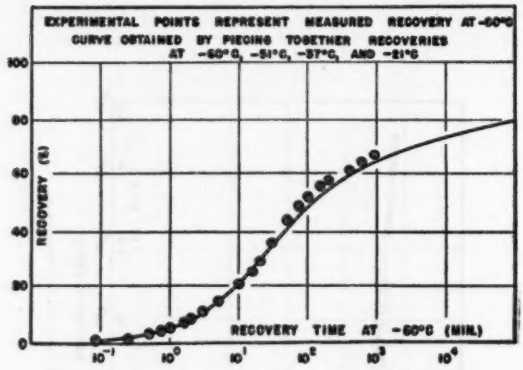

EXPERIMENTAL POINTS REPRESENT MEASURED RECOVERY AT -60°C
CURVE OBTAINED BY FITTING TOGETHER RECOVERIES
AT -60°C, -51°C, -37°C, AND -21°C
RECOVERY (%)
RECOVERY TIME AT -60°C (MIN.)

FIG. 4.—Recovery from equilibrium deformation of Hevea (35.6-lb./sq. in. load).

Figures 6–8 show joined together recovery curves at even decade temperature intervals on motor mounting-type stocks of Neoprene-GN, Butyl rubber, and Butaprene. (Formulas are given in Reference 3.) Each curve is characteristically sigmoidal. Only the Neoprene-GN, however, shows the sharp increase in deformation with time that was evident in the Hevea stock. The Neoprene-GN curve also shows a slight upturn at high temperatures, possibly because of the disappearance of a slight degree of crystallization.

An application of the above empirical formula to the data is shown in Table I, which gives the constants and derived test temperatures. These calculations were based on the time required for 50 per cent recovery at each temperature. The constant C_β is affected by the degree of recovery chosen. The constants C_α and b appear to be properties of the material tested and are independent of the reference point. Values of T and $\log t_c$ were substituted in Equation (1) at three different temperatures for which the data were on the smooth curve. Solution of the resulting simultaneous equations gave the constants C_α, C_β, and b. The derived test temperatures given in Table I were obtained by an application of Equation (1) to data obtained at even decade temperature intervals. If the data shown in Figures 6–8 had been obtained at the derived test temperatures, then all experimental points should have been on the curves, as they were in Figures 3 and 5.

The interdependence of time, temperature, stress, and strain in the viscoelastic phenomena is well known. Mullins[4] recognized the need for a test that would use time as a parameter in determining low-temperature serviceability.

TABLE I

VALUES OF EMPIRICAL PARAMETERS IN EQUATION (1) FOR 50 PER CENT RECOVERY FROM EQUILIBRIUM SHEAR DEFORMATION OF VARIOUS ELASTOMERS

Stock	C_α	C_β	b	Derived test temp. (° C)
Hevea	1780	−17.5	122	−60, −51, −37, −21, 2, 31
GR-S	3121	−19.1	100	−50, −40, −27, −20, −4, 30
Neoprene-GN	480	− 7.52	193	−40, −32, −20, 0, 40[a]
Butyl rubber	5040	−23.52	33	−60, −46, −38, −30, 0, 40
Butaprene	720	− 8.82	183	−30, −18, −10, 0, 30

[a] This is the derived test temperature for the material in the same crystalline state as it was at lower temperatures. In the test made at 30° C, some of the crystals had probably melted, resulting in a higher recovery than that calculated. This same singularity appeared in the creep curves for Neoprene-GN.

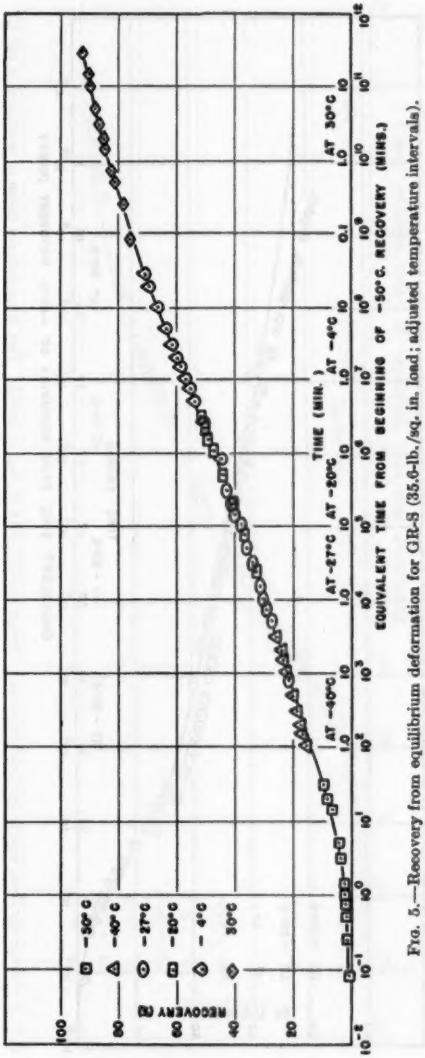


FIG. 5.—Recovery from equilibrium deformation for GR-S (35.0-lb./sq. in. load; adjusted temperature intervals).

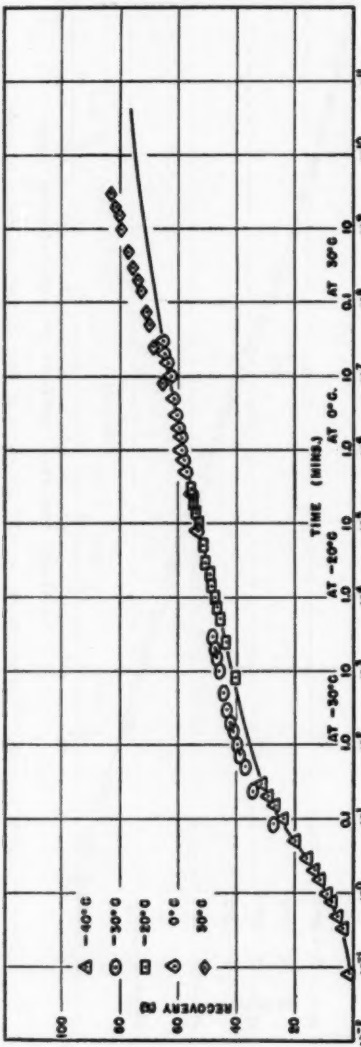


Fig. 6.—Recovery from equilibrium deformation of Neoprene-GN (35.6-lb./sq. in. load). Test temperatures taken at multiples of 10° C.

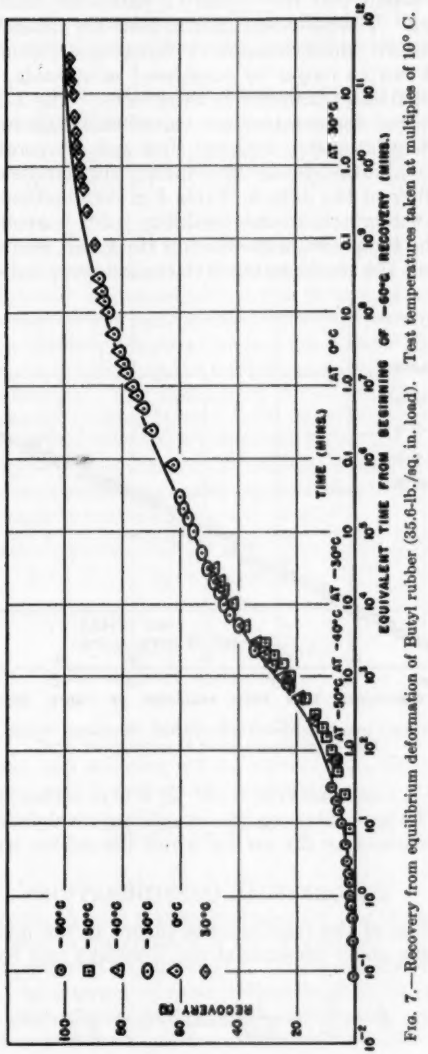


FIG. 7.—Recovery from equilibrium deformation of Butyl rubber (35.6-lb./sq. in. load). Test temperatures taken at multiples of 10° C.

He also stated the need for a simple expression relating time with modulus. Many of the low temperature tests, such as Gehman's torsion test[5], the Young's modulus test of Conant and Liska[6], and the cold compression set test[7] recognize time only to the extent that they specify a particular loading time in making their measurement. The above-mentioned tests are valuable in that they give the temperature below which, because of change in a particular physical property, the product can no longer be considered serviceable. However, time is not directly included as a parameter in these tests. The T-50 test[8] is arbitrary in that both time and temperature are varied simultaneously. Equation (1) does give a simple relationship between time and temperature, thus enabling time to be used as a parameter in determining low temperature serviceability.

The applicability of the data in Table I in conjunction with Equation (1) to determine a low temperature serviceability index is evident. For example, one can obtain the temperature at which a stock will recover 50 per cent in 1 min. On this basis the stocks tested give the following indices: Hevea −49.5°

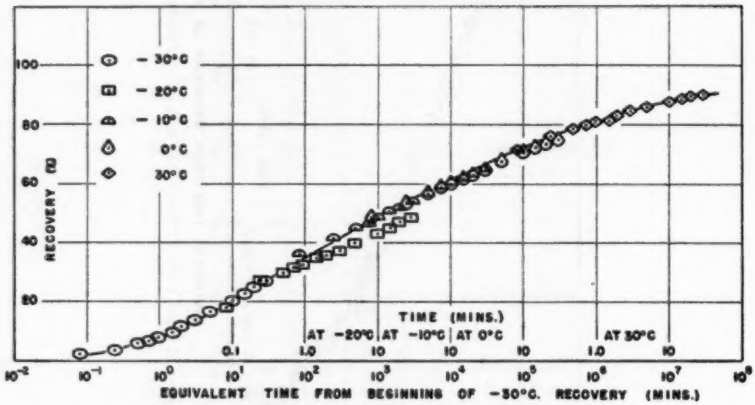


FIG. 8.—Recovery from equilibrium deformation, Butaprene, 35.6-lb./sq. in. load. Test temperatures taken at multiples of 10° C.

C; GR-S −10° C; Neoprene-GN −16° C; Butyl rubber −26° C; and Butaprene −6° C. The particular conditions selected for defining the index would of course, be determined by the use for which the rubber was intended.

THEORETICAL CONSIDERATIONS

In an application of the reaction-rate theory of the mechanical properties of polymers to creep under constant stress, Tobolsky and Eyring[9] arrive at the equation:

$$S = \frac{f}{G_1} + \frac{1}{B_2 G_1} \ln A_2 B_2 G_\mu + \frac{1}{B_2 G_1} \ln t \qquad (2)$$

where S = strain in the specimen; f = total stress; G_1 and G_μ are appropriate elastic moduli associated with strains of the primary and secondary network bonds; and t = duration of creep experiment. The quantities A_2 and B_2 are defined by the equations:

$$A_2 = 2n_2\lambda_2(kT/h) \exp(-\Delta F/kT) \qquad (3)$$

and

$$B_2 = \lambda_2/2N_2kT \tag{4}$$

where k and h are Boltzmann's and Planck's constants, respectively; T is the absolute temperature; F is the free energy of activation for the deformation process; and n_2, λ_2, and N_2 are theoretical quantities related to the unit or elementary process.

If Equation (2) is written out in full and certain terms are cancelled, where possible, we arrive at the equation:

$$S = \frac{f}{G_1} + \frac{2NkT}{G_1\lambda_2}\left[\ln\left(\frac{2n_2\lambda_2}{h}\cdot\lambda_2\frac{G_\mu t}{2N_2}\right) - \frac{\Delta F}{kT}\right] \tag{5}$$

where k and h are well recognized as universal constants. Furthermore, we shall accept the material and structural characteristics, G_1, G_μ, λ_2, and ΔF as being independent of time and temperature. The parameter N_2, however, Tobolsky and Eyring have deduced, decreases with a rise in temperature, though they do not give an expression for the relationship. We shall assume that the inverse variation of N_2 with absolute temperature is a good approximation, and also, that n_2 effectively varies inversely as the temperature through the range covered by the present experiments. The assignment of this functional dependence to N_2 and n_2 is admittedly quite arbitrary from the theoretical point of view. However, if the network of secondary bonds can be regarded as behaving like an ideal gas, the assigned dependence on T becomes entirely reasonable, for N_2 represents the number of secondary bonds per unit area, while n_2 is the number of elementary deformation processes per unit length[10].

Thus we obtain for the viscoelastic component of the deformation:

$$S_v \equiv S - f/G_1 = C_1 \log C_2 t - C_3/T \tag{6}$$

involving the three parameters:

$$\begin{aligned} C_1 &= \text{const.}\cdot 2.30(2k/G_1\lambda_2) \\ C_2 &= \text{const.}\cdot \lambda_2^2 G_\mu/h \end{aligned} \tag{7}$$

and

$$C_3 = \text{const.}\cdot 2\Delta F/G_1\lambda_2$$

By rearranging terms, and selecting a fixed value for S_v, Equation (6), placing $t = t_c$, may be written with a new set of constants:

$$\log t_c = (C_\alpha/T) + C_\beta \tag{8}$$

where

$$C_\alpha = C_3/C_1; \quad C_\beta = (S_v/C_1) - \log C_2.$$

Equation (8) is seen to bear a close resemblance to the empirical Equation (1), the difference being in the absence of the "correction" term, b on the temperature T, which appears in Equation (1). The presence of the b in the empirical equation may be interpreted as an indication that the activation energies for the deformation processes involved in these experiments are not independent of temperature, but rather, are functions of temperature, of a form which gives decreasing values with increasing temperature:

$$\Delta F = \text{const. } T/(T - b) \tag{9}$$

Evidence for the temperature dependence of the activation energy for flow in liquids has been recognized by Ewell[11], though in this case indications are that the activation energy was an increasing function of temperature.

SUMMARY

An explicit relationship is set forth for the time-temperature dependence of the viscoelastic phenomena in superelastic polymers. An empirical equation that was found to represent adequately the above-mentioned relationship over the entire multiple-temperature curve is of the form: $\log t_c = [C_\alpha/(T - b)] + C_\beta$. Experimental verification is given for the equivalent influence of time and temperature on the creep and recovery of compounds based on Hevea, GR-S, Neoprene-GN, Butaprene, and Butyl rubber. A comparison of the empirical equation with that of a theoretical reaction-rate equation of Tobolsky and Eyring indicates a temperature dependence of the energy of activation.

ACKNOWLEDGMENTS

The constructive interest of George R. Thurman, and his discussions with the authors, have produced valuable suggestions. The encouragement of the officials of the Firestone research organization, and their coöperation in making possible this contribution, is gratefully acknowledged.

REFERENCES

[1] For a review of these studies, see Leaderman, "Elastic and Creep Properties of Filamentous Materials and Other High Polymers," Textile Foundation, Washington, 1943, pp. 30, 75.
[2] Tobolsky and Andrews, *J. Chem. Physics* **13**, 3 (1945).
[3] Conant, Hall and Thurman, *J. Applied Physics* **20**, 526 (1949).
[4] Mullins, *Trans. Inst. Rubber Ind.* **21**, 247 (1945).
[5] Gehman, Woodford and Wilkinson, *Ind. Eng. Chem.* **329**, 1108 (1947).
[6] Conant and Liska, *J. Applied Physics* **15**, 767 (1944).
[7] Morris, Hollister, and Mallard, *India Rubber World* **112**, 455 (1945).
[8] McCortney and Hendrich, *Ind. Eng. Chem.* **33**, 579 (1941).
[9] Tobolsky and Eyring, *J. Chem. Physics* **11**, 125 (1943).
[10] It may be remarked that attempts, before Equation (1) was adopted for trial, to fit to the experimental data a working equation based on the assumption of the temperature independence of N_2 and n_2 proved unsatisfactory.
[11] Ewell, *J. Applied Physics* **9**, 252 (1938).

THE STRUCTURE OF ELASTOMERS AND THEIR REACTIVITY *

A. S. Kuz'minskiĭ and N. N. Lezhnev

Scientific Research Institute of the Rubber Industry, U.S.S.R.

It has not yet been ascertained what constituent parts within the structure of various elastomers have the greatest influence on the reactivity of the elastomers. There are indications that the side chains[1], the presence of methyl groups acting as substitutes[2], and differences in spatial configurations[1], etc., all have definite effects. The present authors have investigated the oxidation of several different elastomers at different temperatures. The experiments were carried out both in the presence and in the absence of an inhibitor (phenyl-β-naphthylamine). The elastomers and the inhibitor were first carefully purified.

The kinetics of autoxidations were studied volumetrically by means of an apparatus already described by one of the authors[3]. A chainless molecular introduction of oxygen into the double bonds of the elastomer in the presence of the inhibitor was studied with the aid of our own previously described inhibitor methods[4]. The study included the oxidation of butadiene elastomers containing different distributions of double bonds in the main and side chains, divinylstyrene rubber, and the hydrocarbons of natural rubber and gutta-percha. These products are distinguished by their different degrees of unsaturation, the number of side chains, the number of double bonds in both their main and side chains, the length of their molecular chains (the mean molecular weight), and their spatial configurations.

Figures 1 and 2 show the kinetic curves of absorption of oxygen during autoxidation and the consumption of inhibitor during its participation in the oxidation process. The following conclusions may be drawn from these figures.

1. The elastomers may be listed according to their rates of oxidation on the basis of a particularly striking characteristic which is wholly independent of the length of the molecular chains, spatial configurations, or presence of low-activity groups (aromatic rings in divinylstyrene polymer, etc.), *viz.*, the number of double bonds in the main chains[5]. This is characteristic of oxidation in the presence of an inhibitor as well as of autoxidation.

2. The kinetics of the consumption of inhibitor conforms to a linear law, independent of the nature of the polymer. The rate of consumption of inhibitor (measured by the slope of the kinetic curves on the time axis) corresponds to the rate of the initial reaction between the oxygen and polymer (the beginning of the oxidation process)[6], since in the presence of the inhibitor the chain reaction has hardly commenced[4].

Table 1 shows the rates of initiation of oxidation w_i and their constants k_i for two temperatures, calculated from the inhibition data[7]. The number of double bonds was practically constant, as was the amount of oxygen dissolved

* Translated for Rubber Chemistry and Technology by Alan Davis from the *Reports of the Academy of Sciences*, U.S.S.R., Vol. 70, No. 6, pages 1021–1024, February 21, 1950.

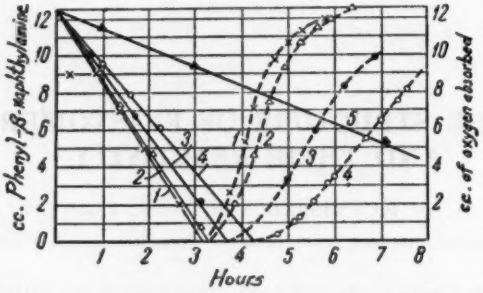


FIG. 1.—Kinetic curves consumption of inhibitor and curves of absorption of oxygen after complete exhaustion of the inhibitor. The temperature was 120°, and the original concentration 12.8 millimoles of inhibitor per mole of elastomer.

1. Gutta-percha hydrocarbon.
2. Natural-rubber hydrocarbon.
3. Divinylstyrene rubber.
4. Butadiene rubber containing 60% double bonds in its main chains.
5. Butadiene rubber containing 20% double bonds in its main chains.

(the rate of diffusion of oxygen in a film 30–50 μ is many times greater than the rate of its consumption during inhibited oxidation).

Plotting the relation between the rate of oxidation (w_i or k_i) of the polymer in the presence of the inhibitor (at 120° for example) and the corresponding content of double bonds in the main chains, we observe the regularity shown in Figure 3.

The nearly linear relation (within the experimental limits of the available data on the distribution of double bonds in the main and side chains) indicates that the rate of initiation of the reaction varies directly with the number of double bonds in the main chains of the rubber molecules. This basic rule includes the effects of all the other factors.

No appreciable difference is observed in the rates of oxidation of the hydrocarbons of natural rubber (molecular weight $\cong$ 200,000; *cis*-configuration at identity periods) and of gutta-percha (molecular weight $\cong$ 28,000; *trans*-configuration) within the limits of the high accuracy of the inhibition data, whereas a significant difference is observed in the oxidation of butadiene polymers. This is explained by the dissimilar distribution of double bonds in the main and side chains.

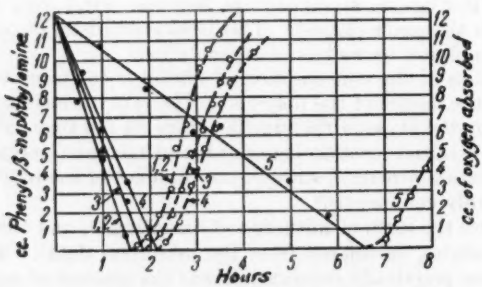


FIG. 2.—The kinetic curves of consumption of inhibitor and the curves of the oxygen after complete consumption of the inhibitor. Temperature was 130°. The initial concentration of the inhibitor was 12.5 millimoles per 1 mole of rubber. The designations are the same as in Figure 1.

TABLE 1

Polymers	Percentage content of double bonds in main chains according to ozonolysis data	$w_i \cdot 10^7$ 120°	$w_i \cdot 10^7$ 130°	$k_i \cdot 10^7$ 120°	$k_i \cdot 10^7$ 130°
Butadiene	20	2.34	4.70	33.0	66.0
	60	8.10	18.20	112.5	256.3
Divinylstyrene	75	8.70	18.27	122.8	257.3
Butyl rubber	100	~0.20	~0.45	~3.0	~7.8
Natural rubber (hydrocarbon)	100	10.04	20.31	176.1	357.3
Gutta-percha (hydrocarbon)	100	10.10	20.01	177.2	354.0

From the rates of initiation of oxidation at different temperatures, it is easy to calculate the energy of activation.

The threshold energy for the introduction of oxygen into the double bonds of the main chains is 21–23 kcal. per mole for all the polymers investigated.

The double bonds in the side chains under these conditions are practically inactive. In the region of autoxidation, they are partially oxidized. The energy of activation (calculated from the kinetic data) of the absorption of oxygen into the double bonds of the side chains (calculated from the kinetic data) is 26–28 kcal. per mole.

The kinetic curves of consumption of inhibitor in the oxidation of Butyl rubber reach a breaking point; this rubber contains so few double bonds that in its properties it occupies an intermediate position between unsaturated and saturated polymers.

With the inhibition of oxidation of the latter elastomers, a characteristic break in the consumption curves of the inhibitor is observed. Kuz'minskiĭ and Klutrov showed that the cause of this broken line in the oxidation of polyisobutylene parallels the change in molecular weights of the oxidized polymer. Here a characteristic threshold is reached, below which the inhibitor is not consumed. The location of this threshold depends on the temperature of the experiment. Investigation of this phenomenon makes it possible to establish

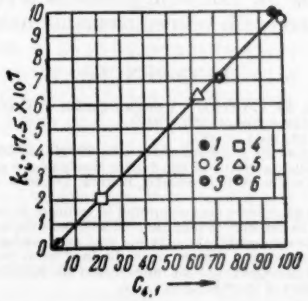


FIG. 3.—Relation between the values of the initiation constant k_i and the double bond content in the main chains $C_{4,1}$.

1. Gutta-percha hydrocarbon.
2. Natural rubber hydrocarbon.
3. Divinylstyrene polymer.
4. Butadiene polymer containing 20% double bonds in the main chains.
5. Butadiene polymer containing 60% double bonds in the main chains.
6. Butyl rubber.

a relation between the stability of the chains and their length. At every temperature there is a definite molecular weight which is stable at that temperature.

The same phenomenon is observed in the oxidation of Butyl rubber containing an inhibitor. Up to the point of establishment of a constant molecular weight, the molecules of the single bonds react faster with oxygen than those of the double bonds; when this condition is reached, oxidation continues more slowly because of the double bonds in the main chain.

From this it follows that the stable mean molecular weight is a result of the presence in the system of varying lengths of polymer chain fractions; we may assume that long chains react earlier than do short chains.

Thus in the case of ordinary unsaturated polymers, just as in the case of saturated polymers, the specificity of the more highly polymeric molecules (that is, of the long chains), is maintained. The long bonds in the main chains are more active than those in the side chains. The rate of absorption of oxygen into the main chains at 80° to 130° C is several orders greater than that into the side chains.

FIG. 4.—Kinetic curves of consumption of inhibitor in the oxidation of polyisobutylene (2) and Butyl rubber (1). The temperature was 110°; 0.5% by weight of phenyl-β-naphthylamine was introduced.

Since the process of autoxidation soon causes a profound change in the mechanical properties of the polymers when vulcanized, the polymers have technical value only until the commencement of autoxidation, that is, in that period when only the initiation process is taking place. This initiation is effected with oxygen in the presence of the inhibitor. Accordingly, the reaction is confined almost exclusively to the double bonds of the main chains.

The established relation between the relaxation properties of elastomers and the distribution of double bonds in their molecules was observed by the present authors, not only for oxidation processes involving oxygen, but also the reaction of elastomers with ozone, inorganic acids, and other chemical agents.

REFERENCES

[1] Cole and Field, *Ind. Eng. Chem.* **39**, 174 (1947); RUBBER CHEM. & TECHNOL. **20**, 747 (1947).
[2] Mesrobian and Tobolsky, *J. Polymer Sci.* **2**, 463 (1947).
[3] Kuz'minskiĭ, *J. Org. Chemistry* **18**, 1504 (1948).
[4] Kuz'minskiĭ and Lejnev, *Reports to the Academy of Sciences* **69**, No. 4 (1949).
[5] The first observation of the distinct activity of the double bonds of the main and side chains of a sample of butadiene polymer was made by Kuz'minskiĭ, Shaniu, Degteva, and Lapteva in 1946 (see *Colloid J.* **10**, B, 1, 26 (1948)).
[6] The rates of increase in concentration were also computed in terms of moles of a structural unit containing one aliphatic double bond in one liter of polymer. The rates were computed in cc. per second. The aromatic component of the divinylstyrene polymer was disregarded as superfluous.
[7] The quantity w is not a single constant. Values were obtained from the inhibition data which approximated the true values, and indicated that the molecules of the inhibitor react in certain stoichiometric ratios with the initial centers of increasing activity.

THE ROLE OF INTERMOLECULAR FORCES IN THE MECHANISM OF HIGH ELASTIC DEFORMATION. II. RELAXATION PROPERTIES OF NATURAL RUBBER AND ITS BROMINATION PRODUCTS.*

B. Dogadkin and M. Reznikovskiĭ

Department of the Chemistry and Physics of Rubber, Lomonosov Institute of Fine Chemistry and Technology, Moscow, U.S.S.R.

In the preceding communication[1], we investigated the mechanism of relaxation phenomena accompanying the high elastic deformation of polymers and showed that these processes are the result of a regrouping of the structural elements of the molecular chains accomplished by the intermolecular forces. The following differential equation was suggested:

$$\frac{d(\sigma - \sigma\sim)}{dt} = (E_0' - E\sim)\frac{d\epsilon}{dt} - \frac{\sigma - \sigma\sim}{\tau} \tag{1}$$

which, together with the expression:

$$\tau = \tau_0 \exp \frac{U_0 - \frac{V}{2E_1}\sigma_1^2}{kT} \tag{2}$$

may be used as an approximately quantitative description of high elastic polymers.

Equations (1) and (2) are accurate for the temperature, rate of deformation, and time of observation when the initial modulus E_0' has a characteristic low value (indicating a high elastic mechanism of deformation) and when the chemical bonds are not broken, so as to cause a permanent structural change as a result of deformation. In these expressions, σ is the instantaneous stress, $\sigma\sim$ the average stress, ϵ is the deformation, t is the time, E_0' is the initial modulus, $E\sim$ is the average modulus; and τ is the time of relaxation, which is itself a function of the unbalanced pressure. In Equation (2), τ_0 is a constant which is unaffected by the experimental conditions, U_0 is the energy of the activation of the elementary structural relaxation, V is the kinetic unit of relaxation, k is the Bolzmann constant, T is the absolute temperature, and $E_1 = E_0' - E\sim$ is the socalled unbalanced modulus.

To illustrate these statements, and to establish the applicability of Equations (1) and (2), certain experimental data were introduced concerning the relaxation of stress in films of natural rubber (smoked sheet).

The present paper is an interpretation and discussion of experimental data obtained from investigations of the relaxation properties of natural and brominated rubber. These investigations were undertaken in connection with the

* Translated for Rubber Chemistry and Technology by Alan Davis from *Colloid Journal*, Vol. 12, No. 2, pages 102–111 (1950).

fundamental problem of studying the importance of intermolecular forces in the mechanism of high-elastic deformation. Inasmuch as the addition of bromine is not accompanied by any basic molecular disintegration or synthesis, it leads to a product distinguished from the original only by the increased concentration of polar groups, necessitating an increase in intermolecular energy in general.

BROMINATED RUBBER AND ITS PROPERTIES

The reaction of natural rubber with bromine has been thoroughly investigated in connection with the determination of the rubber hydrocarbon content[2].

If bromination takes place in solution at a low temperature (that of ice), almost quantitative addition of bromine to the double bonds takes place, and the accompanying splitting off of the halide acid, which occurs especially in chlorination, is hardly appreciable, and, consequently, the structure of the molecular chains remains practically unchanged.

Bromination was carried out in a dilute solution containing 0.3 gram of rubber per 100 cc. of solution. To prepare the bromination solution, 2 grams of iodine was dissolved in 100 cc. of distilled air-free carbon tetrachloride, the solution was filtered, and 5 cc. of technically pure bromine (which had been pruified by double distillation over potassium bromide) was added. The bromine solution in three times the theoretical quantity was added dropwise during thirty minutes, while the low temperature was maintained with ice and the mixture stirred with an electromagnetic mixer. After addition of all the bromine, the mixture was kept cold for two hours more, after which the brominated rubber was precipitated by a mixture of methanol and benzene. A film of brominated rubber, like the original smoked sheet, was obtained by evaporating the solvent from the chloroform solution on a cellophane surface.

The brominated rubber was a polymer, which was lustrous at room temperature, and was only slightly soluble in ordinary organic solvents. The best of the solvents tried was chloroform, in which a bromide concentration of two per cent was reached. The bromine content, determined by the method of Fitz, Schrauber, and Burkhardt[3], did not exceed eighty-five per cent of the theoretically computed value for a dibromide. The determination of the molecular weight, by light-scattering of the solution, was carried out by the method described by Dogadkin and Sobolev[4]. The molecular weight of the brominated rubber was 400,000. A comparison of this value with the molecular weight of the original rubber (213,000) confirmed the assumption on which the present work was based, *viz.*, that bromination, carried out with the necessary precautions, does not cause either an essential disintegration or build-up of the original polymer. x-Ray studies were made in the NII x-ray laboratory of the tire industry in order to determine the effect of bromination on the crystallizing properties of rubber.

Unstretched laboratory specimens and specimens stretched up to elongations of 100, 200, and 300 per cent were studied. x-Ray photographs indicated the absence of a crystalline phase in any of these specimens.

METHOD AND EXPERIMENTAL DATA

As has already been shown[1], the most suitable way of experimentally verifying Equations (1) and (2) and of determining the value of the constants is the study of the relaxation of stress with constant deformation and temperature.

In this case where ϵ is constant and $\frac{d\epsilon}{dt} = 0$, Equation (1) appears as:

$$\frac{d\sigma}{dt} = -\frac{1}{\tau}(\sigma - \sigma\sim) \tag{3}$$

However, introducing the symbols:

$$\tau^* = \tau_0 \exp \frac{U_0}{kT} \tag{4}$$

and

$$\beta = \frac{V}{2E_1kT} \tag{5}$$

Equation (2) may be written more simply:

$$\tau = \tau^* \exp - \beta(\sigma - \sigma\sim)^2 \tag{6}$$

where τ^* and β, as follows from Equations (4) and (5), are constant for a given deformation and temperature. Thus, taking the logarithm of Equation (6), we have:

$$\log \tau = \log \tau^* - \frac{\beta}{2.3}(\sigma - \sigma\sim)^2 \tag{7}$$

which expresses the linear relation between the square of the unbalanced pressure and the logarithm of the time of relaxation. The values of the time of relaxation corresponding to the different instantaneous values of the unbalanced pressure may be obtained from the stress relaxation curves by the method described in the previous article[1]. Here we shall limit ourselves to describing the methods of drawing the curves of the relaxation of stress and determining the equilibrium stress $\sigma\sim$ for a given deformation and temperature.

The apparatus for the mechanical investigations was the precision dynamometer of the Mendeleyev MOVKhO equipment laboratory. This apparatus is used in the investigation of deformation brought about by uniform pressure. It generally measures the elongation within 0.01 mm. and the deforming force within 0.1 per cent of its maximum value in the experiment. The deformed specimen, fastened in the dynamometer clamps, is put inside a double-walled glazed cylindrical jacket similar to a Dewar flask. The jacket is connected to an ultrathermostat by rubber tubing, which furnishes continuous circulation to the temperature-controlled liquid, so that a constant temperature is maintained around the deformed specimen. The desired temperature is maintained within $\pm 0.2°$ C.

The stress relaxation was studied at different temperatures between 0° and 80° and for different initial deformations from 50 to 600 per cent. Typical curves are shown in Figures 1 and 2.

To find the time of relaxation τ from curves such as those in Figures 1 and 2 in accordance with Equation (3) let $\sigma\sim$ equal the equilibrium stress at the given temperature and deformation. The latter quantities, by definition, do not depend on the way in which the given condition is achieved.

The case described gives one criterion to distinguish the true equilibrium from the apparent equilibrium. A similar apparent equilibrium is observed when the rate of the spontaneous processes is so small that changes which occur during the observed period of time are inappreciable. If the stress relaxation

in a deformed sample of brominated rubber at room temperature is observed, for example, after 3–4 hours, an apparent equilibrium is reached, and no further decrease in stress is observed. Nevertheless, it is easy to show that the condition referred to is unbalanced.

Actually, if the temperature is raised 10 to 20° C, a further decrease in the pressure is observed, and after 20–30 minutes a new equilibrium is reached which corresponds to the new temperature.

If, however, the sample is again cooled to its original temperature, the original stress is not restored. Furthermore, a new, slight increase in the temperature is now observed. The obvious explanation is that an increase in temperature, by accelerating the relaxation processes, causes the applied stress to approach the true stress. The higher the temperature at which the initial equilibrium is reached, the less evident is this effect. At a temperature of 70° C, it is already practically inappreciable; consequently it can be concluded that the equilibrium reached on the relaxation of the stress under these conditions approximates the true equilibrium.

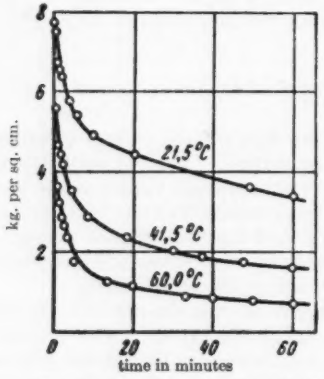


FIG. 1.—Stress relaxation at constant 100% elongation and at different temperatures for films of smoked sheet rubber.

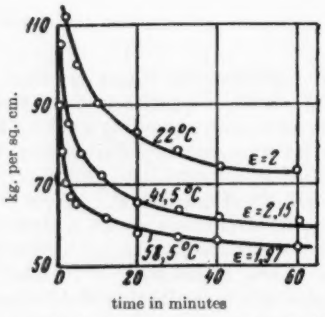


FIG. 2.—Stress relaxation at constant 200% elongation and at different temperatures for films of brominated rubber.

The calculations above were used with the following method of determining the conditions of equilibrium.

The sample was deformed at the given temperature, after which at constant deformation the relaxation of stress to the point of apparent equilibrium was measured. The temperature was then raised to 70° C, and at this point the greatest relaxation during a 30–40 minute period was measured. After this time, apparent equilibrium was again reached.

When the temperature was lowered to its original value, we found the stress which, within a reasonable degree of accuracy, may be considered the equilibrium stress; in fact, when the experiment was repeated, that is, when the temperature was first raised and then lowered, the initial and final stress values practically coincided. This proved the equilibrium character of the observed length. Table 1 gives data illustrating the use of the method described and the results obtained.

As is evident in Table 1, the equilibrium stresses for smoked-sheet rubber are practically equal to zero.

TABLE 1

DETERMINATION OF THE EQUILIBRIUM STRESS AT DIFFERENT TEMPERATURES FOR SMOKED-SHEET RUBBER AND BROMINATED RUBBER (200% ELONGATION)

Material	Temperature (° C)	Stress at given temperature (apparent equilibrium) (kg. per sq. cm.)	Equilibrium stress after heating to 70° C (kg. per sq. cm.)	Equilibrium stress at given temperature (kg. per sq. cm.)
Smoked sheet rubber	5	7.8	0.0	0.0
	22	2.9	0.0	0.0
	40	1.9	0.0	0.0
	60	0.2	0.0	0.0
	70	0.0	0.0	0.0
Brominated rubber	20	64.1	51.2	50.0
	40	58.0	52.0	51.5
	60	53.5	52.2	52.0
	70	51.6	51.5	51.5

It is interesting to note that, despite apparently complete stress relaxation in the deformed test-specimens of smoked sheet rubber, they nevertheless almost completely recovered their original lengths, as was proved by determinations of the residual deformation.

Returning to the experiments on stress relaxation, we see that, by knowing the values of the equilibrium stress $\sigma\sim$, and by using the method of finite differ-

TABLE 2

VALUES OF τ^* AND β OBTAINED FROM EXPERIMENTS ON THE STRESS RELAXATION AT DIFFEERNT TEMPERATURES AND ELONGATIONS

Temperature (° C)	Elongation	log τ^*	τ^* (min.)	$\beta/2.3$ (kg.$^{-1}$cm.^{4})	Temperature (° C)	Elongation	log τ^*	τ^* (min.)	$\beta/2.3$ (kg.$^{-1}$cm.^{4})
				Smoked Sheet					
22.5	0.62	2.8	632	0.118	61.5	0.46	1.85	71	0.267
	1.03	3.1	1260	0.055		0.93	1.8	63	0.154
	1.5	3.0	1000	0.040		2.08	1.9	79.5	0.046
	1.99	2.9	795	0.033		2.98	1.95	89.2	0.045
	3.14	3.3	1998	0.0188					
	4.97	3.35	2285	0.010	80.0	0.67	1.55	35.7	0.312
						1.02	1.40	25.1	0.119
40.0	0.54	2.4	251	0.134					
	1.18	2.35	223	0.087	5.0	0.54	3.9	7950	0.182
	2.15	2.5	316	0.045		0.85	3.55	3570	0.072
	3.08	2.2	159	0.020		2.0	3.5	3160	0.014
	4.98	2.65	447	0.0143					
	6.96	2.85	710	0.0068					
				Brominated Rubber					
22	0.5	1.95	89.2	1.0×10^{-3}	51	2.04	1.70	50.2	1.2×10^{-3}
	0.98	2.10	126.0	5.8×10^{-4}	—	—	—	—	—
	2.0	1.90	79.5	2.2×10^{-4}	58.5	1.07	1.44	27.6	2.2×10^{-2}
	3.0	2.55	355	1.3×10^{-5}	—	1.52	1.55	35.5	1.6×10^{-2}
	—	—	—	—	—	1.97	1.50	31.6	4.4×10^{-3}
41.5	0.48	1.80	63.2	1.6×10^{-2}	—	2.42	1.70	50.2	5.0×10^{-4}
	0.98	1.84	69.3	9.1×10^{-3}	—	—	—	—	—
	2.15	1.70	50.2	6.5×10^{-4}	80.0	0.52	1.20	15.9	1.5×10^{-1}
	3.02	1.75	56.3	3.6×10^{-5}	—	1.02	1.36	22.9	5.2×10^{-2}
	—	—	—	—	—	1.60	1.30	20.0	6.0×10^{-3}

ences, we can determine the corresponding time of relaxation for any point on the stress-time curve. Converting the values obtained to logarithms of the corresponding squares of the unbalanced stress, we find a linear relation, in accord with Equation (7).

Such linear relations (see Figures 3 and 4) were obtained in all cases, and are of importance as a confirmation of the general theoretical assumptions made in the previous work.

The values of the characteristic constants τ^* and β can be respectively determined by a segment, cut straight along the ordinate axis, and by the tangent of the angle of slope in the graphs of Figures 3 and 4.

The corresponding data are shown in Table 2.

INTERPRETATION OF THE RESULTS

Figures 3 and 4 and the data in Table 2 enable us to draw certain conclusions concerning the change in constants τ^* and β relative to the temperature of deformation[5]. The most interesting fact is that the values of τ^*, which depend on the temperature, do not vary with the deformation, whereas β diminishes quite sharply during the deformation process (see Table 2).

A comparison of this result with Equations (4) and (5) leads to the conclusion that, in the deformation process, the limited factor of relaxation V diminishes significantly, while the energy of activation U_0 remains constant.

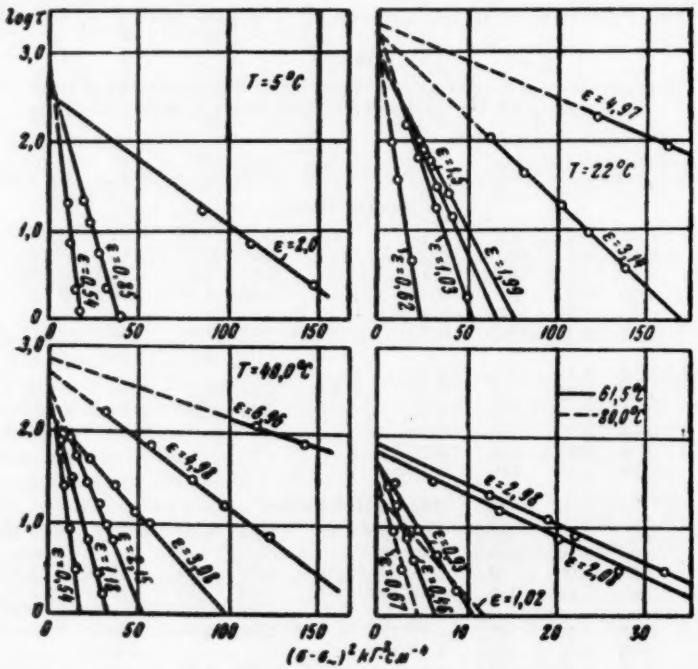


FIG. 3.—Time of relaxation of smoked-sheet rubber as a function of the equilibrium stress at different elongations.

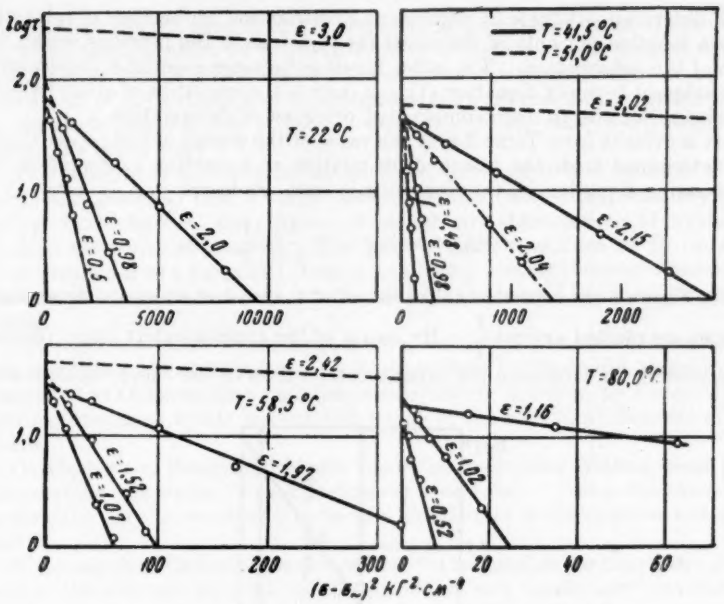


FIG. 4.—Time of relaxation of brominated rubber as a function of the equilibrium stress at different elongations.

If the reaction between the chains of the polymer is considered to be fundamentally indistinguishable from the intermolecular reaction in a low-molecular liquid, then the result obtained must be considered quite unintelligible, since it is impossible to assume that the energy of activation of the internal transposition of a certain unit volume does not depend on the size of this volume.

However, a contradiction which appears difficult to explain from the viewpoint of the theory of the semiliquid structure of polymers can be quite simply explained if the characteristic of a macromolecular reaction is considered to be the presence of definite bonds which set up a sort of network structure possessing only limited stability. The existence of these bonds is due, not to the forces of chemical affinity, but to the chance location of the van der Waals forces of attraction. In this case the energy of activation U_0 depends on the energy of the elementary local bonds, just as the kinetic factor in the relaxation V and the constant β depend on the concentration of bonds in the polymer. A decrease in β in the deformation is caused by an increased concentration of local bonds, resulting from increased activity between the chains, which is governed by their orientation, just as the constancy of U_0 indicates only that the energy of the elementary local bonds does not change during reorientation of the chains.

Thus the idea of the presence of fixed van der Waals bonds between the molecules of polymers, brought forth in the investigations of Dogadkin[6], Jurkov[7], Kargin[8] and others, and also the theoretical observations of London[9] are definitely confirmed in the present work.

It should be mentioned that, in addition to the establishment in the present work of the nature of intermolecular activity, the decrease in the constant β

with deformation (Table 2) requires an investigation of the time of relaxation τ as a function not only of the stress (as was done in the previous work), but also of the deformation. The latter function becomes especially important in any attempt to apply Equation (1), not only to the relaxation of stress (where ϵ constant) but also to more complicated processes of deformation.

It is evident from Table 2 that the value of the energy of activation U_0 can be determined from the temperature relation τ^* according to Equation (4). Converting Equation (4) into logarithmic form, we have:

$$\log \tau^* = \log \tau_0 + \frac{U_0}{2.3k} \cdot \frac{1}{T} \tag{8}$$

In Figure 5 the experimental values of τ^* for smoked sheet and brominated rubber are plotted against $\frac{1}{T}$. By means of the approximately linear relation, it is possible to determine the experimental values of the energy of activation U_0.

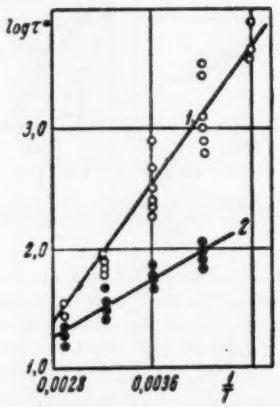


FIG. 5.—Total relaxation τ^* as a function of temperature.
(1) Smoked-sheet rubber. (2) Brominated rubber.

Corresponding calculations of this quantity and the standard grammolecule (mole of "kinetic elements of relaxation") gives values for smoked sheet of 15 to 17 kcal.; and for brominated rubber of 5 to 6 kcal.

The fact that the value of U_0 is lower for brominated rubber than for smoked sheet is easy to explain, since the energy of activation was calculated only for a single bond (a single kinetic element of relaxation).

The positive increase in the general energy of reaction between the chains of rubber is the result of the large number of elementary chains present, as is confirmed by the sharp decrease in the value of the constant β for brominated rubber, as compared with the original smoked sheet. Since the energy of activation of the relaxation process for brominated rubber is the same as the heat of sublimation of hydrogen bromide (5.52 kcal./mole) it may be assumed that the local bonds in rubber bromide depend on the activity of the atoms of bromine. Consequently, although the magnitude of values obtained for U_0 may help somewhat in explaining the nature of the local bonds in the polymers,

this question has not been sufficiently studied at the present time. In particular, these bonds cannot be attributed solely to active groups present in the chains (polar groups governing the formation of hydrogen bonds, etc.) The mechanism of the formation of local bonds is more general, and its understanding demands explanations of general questions of the state of aggregate of rubber-like polymers.

The presence of microcrystalline particles, surrounded by a medium in the amorphous state, so that a single molecular chain may simultaneously pass through both phases of the polymer, is particularly characteristic of crystallizing high-molecular substances. The latter condition enables us to consider the microcrystal as a particular form of local bond, uniting the macromolecules. The energy in any given case is determined from the heat of fusion of the microcrystal.

For polymers which do not crystallize, a similar mechanism of formation of local bonds is evidently possible. In this case these bonds should, therefore, be considered to be amorphous particles, distinguished, however, by a more dense packing, compared to the surrounding region of the structural elements of the chains.

On the basis of the general kinetic theory of condensing systems, these particles may be regarded as "liquid particles in a solid state," just as the surrounding medium may be considered to be in a liquid state of "orientation evaporation"[10].

If the region of "orientation evaporation" is responsible for the elastic properties of the polymer, then the "solid" region acts as a "secondary" juncture or local bond between the molecules of the polymer. The only difference between the case in question and the previous case appears to be that the transition from the solid state to the state of orientation evaporation is not a change in phase in the usual sense.

Indirect confirmation of the accuracy of these assumptions is had by x-ray studies of rubber by Kasatochkin and Lukin[11], who concluded that a so-called "gas phase" is present in rubber on the basis of data on the change in the intensity of an amorphous halo and on interference spots on vulcanization.

CONCLUSIONS

1. With a view to explaining the role of intermolecular forces in the mechanism of high-elastic deformations, the stress relaxation in natural and brominated rubber was studied.

2. The stress relaxation in these substances at temperatures from 5° to 80° C and at different initial deformations is represented by the equation:

$$\frac{d(\sigma - \sigma\sim)}{dt} = (E_0' - E\sim)\frac{d\epsilon}{dt} - \frac{\sigma - \sigma\sim}{\tau}$$

where the relaxation time τ is a function of the stress:

$$\tau = \tau_0 \exp \frac{U_0 - \frac{V}{2E_1}(\sigma - \sigma\sim)^2}{kT}$$

The latter expression makes it possible to determine the energy of activation U_0 of the relaxation process and the kinetic element of relaxation V from the experimental data.

3. The energy of activation U_0 is 15–17 kcal. for smoked sheet and 5–6 kcal. from brominated rubber, and is independent of the degree of deformation.

4. The "kinetic element" of relaxation varies with the degree of deformation, *i.e.*, it diminishes as the latter increases.

5. On the basis of the experimental data, the presence in the polymer of local intermolecular bonds, whose destruction and restoration underlies the relaxation phenomena studied, is indicated.

REFERENCES

[1] Dogadkin, Bartenev, and Reznikovskii, *Colloid J.* **11**, 314 (1949).
[2] Kheraskov, *J. Rubber Industry* **9**, 856 (1935).
[3] Meyer, Analysis and Determination of Structure of Organic Substances, ONTI NKPT, 1935, page 137.
[4] Dogadkin, Sobolev, and Arkhangelskaya, *Colloid J.* **11**, 143 (1949).
[5] The inconstancy of these quantities need not arouse suspicion inasmuch as the character of the intermolecular reaction, which determines the relaxation properties of the polymer, undoubtedly varies not only with the temperature but also with the deformation.
[6] Dogadkin, and Uzina, *Colloid J.* **9**, 97, (1947).
[7] Jurkov, DAN **57**, 493 (1945).
[8] Kargin, Reports of 1st and 2nd Conferences on High Molecular Compounds, AN Press, U.S.S.R.
[9] London, *J. Phys. Chem.* **46**, 315 (1942).
[10] Frenkel, "Kinetic theory of liquids," AN Press, U.S.S.R.
[11] Kasatochkin and Lukin, Reports to 6th Conference on High Molecular Compounds, AN Press, U.S.S.R.

INFLUENCE OF STRUCTURE OF ELASTOMERS ON THEIR PERMEABILITY TO GASES *

G. J. VAN AMERONGEN

RUBBER FOUNDATION, DELFT, HOLLAND

INTRODUCTION

It is a known fact[1] that rubber membranes are permeable to gases and that the rate of permeation is a specific function of a given gas and rubber. We may picture this permeation of gas through rubber as a process in which gas molecules dissolve on one side of the membrane, then diffuse through the rubber to the other side, and there evaporate out of the membrane. Thus the process of permeation is divided into several independent processes, those of solution and evaporation being governed by Henry's law and that of diffusion by the diffusion equation (Fick's law).

The problem to be considered is why a given rubber should possess a given permeability to a given gas. It will at once be evident from what has just been stated that, while studying the problem, the process of solution (or evaporation) and that of diffusion must be dealt with separately. It was shown in earlier investigations[2] on a series of rubber varieties and gases how the chemical structure of the rubber molecules affects the rate at which the gas passes through, and, notably, that the introduction of methyl and polar groups in the polymer molecules and crystallization reduce this rate of diffusion. It was also found that a gas diffuses more slowly as its molecules are larger. The solubility of the gas in the rubber is determined by its tendency to condense and by the interaction between the rubber and the gas molecules.

These views will now be put to the test with reference to another series of rubbers and gases. We shall also see that knowledge of the necessary conditions for low permeability may help to evolve new kinds of rubber of low permeability.

PROCEDURE

The apparatus and methods employed for the determination of permeability, diffusivity, and solubility have already been described[3].

The permeability is derived from the increased pressure in an evacuated space separated from a gas chamber by the membrane under test. The pressure increase is registered by a MacLeod pressure gauge now set to a range up to 1.5 mm. Hg with an accuracy of 0.001 mm. Hg. This pressure gauge ensures considerably greater relative accuracy of measurement than was formerly obtainable.

The permeation coefficient, or permeability Q, follows from:

$$q = QAt(p_1 - p_2)/d \qquad (1)$$

where q = quantity of permeated gas, A = area of the membrane, p_1 and p_2 = pressures on both sides of the membrane, d = thickness of the membrane, and

* Reprinted from the *Journal of Polymer Science*, Vol. 5, No. 3, pages 307–332, June 1950. This paper is Communication No. 99 of the Rubber Foundation, Delft, Holland.

t = time. The quantity of permeated gas follows simply from the pressure increase, the volume, and the temperature of the space under vacuum. The p_1 pressure commonly amounted to approximately 1 atmosphere. The p_2 pressure, which was always less than 1.5 mm. Hg, can be disregarded with respect to p_1. The thickness of the membrane was determined with a Schopper thixometer to within an accuracy of 0.005 to 0.01 mm. As a rule, the determination of the thickness of the membrane is the least accurate part of the permeation test. Besides that, it is very difficult to make membranes of uniform thickness at every point.

The area of the membrane was assumed to be the same as that of the cross-section of the gas chamber, *i.e.*, 30.2 sq. cm. Some slight inaccuracy is here involved, owing to edge effects and the presence of a supporting wire netting. For any measurements made at other than room temperature, the dimensions of the membrane were corrected to allow for thermal expansion. The absolute determination of Q is accurate to within 5 per cent, while the relative accuracy of measurements performed with one and the same membrane at different temperatures or with different gases is within 1 per cent.

The diffusion coefficient, or diffusivity D, is derived from:

$$D = d^2/6\theta \tag{2}$$

where θ is the time lag of the permeation. This lag is related to the time required by the gas to establish a state of equilibrium in the degassed membrane. The time lag is found by extrapolating the pressure increase–time curve to the zero axis after the stationary state has been attained. It can be shown[3] that the stationary stage is reached after a period amounting to three times the time lag, so extrapolation to the zero axis should only be made from measurements taken after that time.

The absolute accuracy of the diffusion coefficient is, again, subject to the accuracy of the measurement of the thickness of the membrane; its relative accuracy is within 1 per cent.

Finally, the solubility, S, follows from:

$$Q = DS \tag{3}$$

Previous investigations[3] have shown that the solubility found by the application of Equation (3) is consistent with the values found by direct measurement.

In the following pages, Q will be expressed as cc. of gas at 0° C and 760 mm. pressure penetrating per second through a membrane with an area of 1 sq. cm. and a thickness of 1 cm. at 1 atm. pressure difference; D will be expressed in sq. cm. per sec., and S in cc. of gas at 0° C and 760 mm. pressure which are dissolved in 1 cc. of material at a pressures of one atmosphere.

MEASUREMENTS

We used membranes of vulcanized rubber of the composition shown in Table I. The majority of the polymers mentioned in this table are commercial products, only polyisoprene, polybutadiene, and isoprene copolymers being especially made by emulsion polymerization[5] for the permeability test. The combined sulfur content of the vulcanized natural rubber was 1.4 per cent. German Perbunan is the equivalent of American Perbunan-26. The thickness of the membranes varied from 0.2 to 2 mm., so for every diffusion process we were able to use a membrane giving a properly measurable time lag. This time

lag should, by preference, be something between five and forty minutes. The gases used were commercial products taken from cylinders[6].

The experiments were first carried out at 25° and 50° C; the results are given in Table II. The figures for butadiene rubber and methyl rubber had been estimated on a previous occasion[3], and have been given here for comparison only. Natural rubber and German Perbunan, which had also been studied before, were now retested under more carefully controlled conditions. Generally speaking, the consistency between the present evidence and that coming from other sources is satisfactory[7].

TABLE I

COMPOSITION OF THE MEMBRANES

Membranes	% N	Mixtures
Natural rubber	—	A
Methyl rubber (dimethylbutadiene bulk polymer)	—	A
Polyisoprene (emulsion polymer)	—	A
74% isoprene + 26% acrylonitrile emulsion copolymer	7.0	A
74% isoprene + 26% methacrylonitrile emulsion copolymer	5.3	B
Polybutadiene (emulsion polymer)	—	A
Perbunan 18 (80% butadiene + 20% acrylonitrile copolymer)	5.4	C
Perbunan (German) (73% butadiene + 27% acrylonitrile copolymer)	7.2	A
Hycar OR 25 (68% butadiene + 32% acrylonitrile copolymer)	8.4	C
Hycar OR 15 (61% butadiene + 39% acrylonitrile copolymer)	10.2	C
Butyl rubber (98% isobutene + 2% isoprene copolymer)	—	D
Polymethylpentadiene (85% 2-methyl- + 15% 4-methyl-1,3-pentadiene copolymer)[4]	—	E
Vulcaprene A (polyesteramide-diisocyanate)	—	F

Mixtures	A	B	C	D	E	F
Rubber	100	100	100	100	100	100
Zinc oxide	5	10	5	3	5	—
Sulfur	1.5	2	1.25	2	1.75	—
Stearic acid	2	1	1.5	1	1	1
Vulkazit-AZ	1.8	—	—	—	—	—
Captax	—	—	—	0.5	—	—
Tuads	—	—	—	1	—	—
Altax	—	—	1.25	—	1	—
Vulcazit-P	1.5	—	—	—	—	—
Phenyl-β-naphthylamine	1	1	1.5	—	—	—
Vulcafor-VHM	—	—	—	—	—	5
Vulcafor-VDC	—	—	—	—	—	0.75
Vulcanization temperature (° C)	142	110	152	155	145	125
Vulcanization time (min.)	30	30	35	45	30	60

The dependence of the various quantities on the temperature will be discussed in the following pages, but we should note now the marked increase in diffusivity and permeability with rising temperature, whereas the solubility of He, H_2, and N_2 increases only slightly, and that of CO_2, C_2H_2, and C_3H_6 decreases with the temperature. The increase in solubility of H_2 and N_2 with the temperature is in agreement with Carpenter's findings[8].

PERMEABILITY

Some hints as to the cause of varying permeability are already afforded by Table II. To obtain a complete picture, it is necessary to split up permeability into its constitutive quantities, *viz.*, diffusivity and solubility.

TABLE II PERMEABILITY Q (IN 10^{-8} CM.^{2} SEC.$^{-1}$ ATM.$^{-1}$), DIFFUSIVITY D

No.	Rubber	Temp. (° C)	H_2			N_2			O_2		
			Q	D	S	Q	D	S	Q	D	S
1	Natural rubber	25	37.4	10.2	0.037	6.12	1,10	0.055	17.7	1.58	0.112
		50	90.8	22.2	0.041	19.4	3.42	0.057	47.0	4.70	0.10
2	Methyl rubber	25	13	3.9	0.033	0.36	0.079	0.046	1.6	0.14	0.114
		50	38	10.5	0.036	2.2	0.41	0.054	7.1	0.61	0.116
3	Polyisoprene	25	37.9	10.03	0.038	5.37	0.94	0.057			
		50	89.0	—	—	17.0	2.53	0.067			
4	Isoprene-acrylonitrile copolymer	25	5.66	2.47	0.023	0.138	0.045	0.031	0.65	0.092	0.071
		50	18.5	6.50	0.029	0.99	0.30	0.033	3.43	0.45	0.076
5	Isoprene-methacrylonitrile copolymer	25	10.36	3.55	0.029	0.455	0.123	0.037	1.79	0.24	0.075
		50	30.0	8.74	0.034	2.43	0.56	0.043	7.52	0.82	0.091
6	Polybutadiene	25	32	9.6	0.033	4.9	1.1	0.045	14.5	1.5	0.097
		50	77	18	0.043	14.5	2.9	0.050	36	3.7	0.097
7	Perbunan-18	25	19.2	6.43	0.030	1.92	0.51	0.038	6.23	0.79	0.073
		50	49.1	14.5	0.034	7.00	1.55	0.045	19.1	2.30	0.083
8	Perbunan (German)	25	12.1	4.50	0.027	0.81	0.25	0.032	2.94	0.43	0.068
		50	33.7	11.1	0.030	3.53	0.98	0.037	10.5	1.44	0.073
9	Hycar OR-25	25	8.97	3.85	0.023	0.46	0.152	0.030	1.78	0.28	0.064
		50	26.3	9.60	0.027	2.30	0.70	0.033	7.08	1.08	0.066
10	Hycar OR-15	25	5.42	2.43	0.022	0.179	0.064	0.028	0.73	0.136	0.054
		50	17.0	6.56	0.026	1.08	0.34	0.032	3.50	0.565	0.062
11	Butyl rubber	25	5.50	1.52	0.036	0.247	0.045	0.055	0.99	0.081	0.122
		50	17.2	4.38	0.039	1.27	0.22	0.057	4.03	0.384	0.105
12	Polymethylpentadiene	25	32.4	—	—	2.09	0.30	0.070	7.62	0.55	0.138
		50	82.1	—	—	9.04	1.28	0.071	25.9	1.98	0.131
13	Vulcaprene-A	25	4.78	2.60	0.018	0.373	0.145	0.026	1.15	0.24	0.048
		50	15.6	7.0	0.022	1.83	0.67	0.027	4.79	0.92	0.052

Butadiene-acrylonitrile polymers provide a clear example of how the nature of the polymer affects the permeability to various gases, as demonstrated in Figure 1. From it we see that acrylonitrile strongly reduces the permeability of butadiene copolymers to a given gas; in fact, with a sufficient acrylonitrile content the material reaches even the low permeability of Butyl rubber. We hope to explain why the permeability is thus reduced by the presence of an increasing percentage of acrylonitrile when we discuss diffusivity and its dependence on temperature. What we may say in advance, however, is that it is a general rule that the presence of polar groups in the polymer molecules produces low permeability. As nitrile groups have a very pronounced polar character, their effect in this sense is very great.

There is another general rule, *viz.*, that methyl groups in the polymer molecules bring about low permeability. Accordingly, polydimethylbutadiene, having one more methyl group per monomeric unit than natural rubber, has a low permeability. Butyl rubber likewise owes this quality to the many methyl groups with which it is enriched.

The permeability of polybutadiene, on the other hand, is little different

(IN 10^{-6} CM.^{2} SEC.$^{-1}$), AND SOLUBILITY S (IN CC. (N.T.P.) PER CC. AT 1 ATM.)

	CO_2			He			C_3H_8			Cyclopropane		
No.	Q	D	S	Q	D	S	Q	D	S	Q	D	S
1	99.6	1.10	0.90	23.7	21.6	0.011	75.5	0.467	1.62	192	0.180	10.7
	221	3.50	0.63	52.3	38.0	0.014	195	1.63	1.20	473	0.72	6.6
2	5.7	0.063	0.91	11								
	24	0.36	0.67	27								
4	3.3	0.031	1.07	5.93	8.01	0.0074						
	16.9	0.203	0.83	16.1	15.1	0.0107						
5	10.8	0.091	1.20									
	40.4	0.444	0.91									
6	105	1.05	1.00									
	200	2.8	0.72									
7	48.2	0.425	1.13	12.9	15.5	0.0083						
	120.8	1.42	0.85	31.2	26.6	0.0117						
8	23.5	0.190	1.24	9.32	11.7	0.0080	18.9	0.0764	2.48			
	67.9	0.77	0.88	23.4	23.0	0.0102	68.3	0.382	1.79	59.3	0.141	4.2
9	14.1	0.107	1.32	7.50	11.2	0.0067						
	45.9	0.515	0.89	19.6	22.1	0.0089						
10	5.67	0.038	1.49	5.20	7.92	0.0066						
	22.4	0.221	1.01	14.2	16.2	0.0088						
11	3.94	0.0578	0.68	6.40	5.93	0.011	1.28	0.0203	0.63			
	14.3	0.276	0.52	17.3	12.6	0.014	5.82	0.108	0.54	10.4	0.0224	4.7
12	34.2	—	—									
	100.8	1.48	0.68									
13	14.1	0.094	1.50									
	48.2	0.44	1.10									

from that of natural rubber, though the absence of methyl groups would have led one to expect a greater permeability. It is certain, however, that this polymer does not consist of pure 1,4-polybutadiene, but is polymerized in the 1,2-position to the extent of at least 20 per cent, and this makes comparison somewhat difficult. The fact that emulsion polyisoprene has virtually the same permeability as natural rubber goes to prove that this polyisoprene contains isoprene polymerized principally in the 1,4-position.

The realization that both nitrile and methyl groups tend to reduce permeability led to the production of the isoprene-acrylonitrile and isoprene-methacrylonitrile copolymers, which, taking the nitrile content into account, have exceptionally low permeability compared to the corresponding butadiene copolymers (see Table VI). With some gases the permeability of the isoprene-acrylonitrile copolymer is the same as that of Butyl rubber; with others it is even appreciably lower.

For practical convenience we have collected in Table III the permeabilities of various polymers relative to natural rubber. The figures for air were obtained on the reasonable assumption that permeability is an additive property

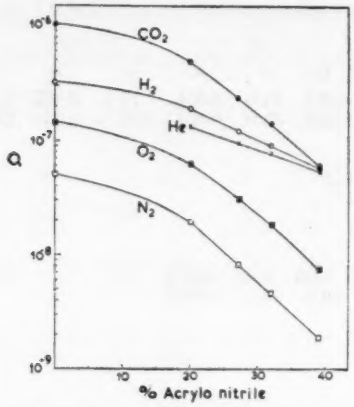


FIG. 1.—Decreasing permeability of butadiene-acrylonitrile copolymers with increasing nitrile content at 25° C.

and that we may therefore write:

$$Q_{air} = \tfrac{4}{5}Q_{N_2} + \tfrac{1}{5}Q_{O_2} \qquad (4)$$

To complete the picture, we have also included in Table III the figures for Buna-S (the equivalent of GR-S), Neoprene, and Thiokol-B, taken from the records of previous experiments[3].

DIFFUSIVITY

The size of the gas molecules determines the rate at which various gases diffuse in a given rubber. Figure 2 shows in a few cases how the rate of diffusion diminishes as the diameter[9] of the gas molecules increases.

The effect of the nature of the rubber on diffusivity is made evident in Figure 3, which gives data on butadiene-acrylonitrile copolymers.

TABLE III

PERMEABILITY OF ELASTOMERS AT 25° C WITH REFERENCE TO NATURAL RUBBER (PURE-GUM VULCANIZATES)

Rubber	H_2	N_2	O_2	CO_2	He	Air
Natural rubber	110	100	100	100	100	100
Polybutadiene	86	80	82	105	—	81
Buna-S	81	78	73	94	74	76
Polymethylpentadiene	87	34	43	34	—	38
Perbunan-18	51	31	35	48	55	33
Perbunan (German)	32	13	17	24	39	15
Neoprene-G	27	14	17	20	—	15
Isoprene-methacrylonitrile copolymer	28	7.4	10.1	10.8	—	8.5
Hycar OR-25	24	7.5	10	14	32	8.5
Polydimethylbutadiene	35	5.9	9.0	5.7	47	7.2
Vulcaprene-A	13	6.1	6.5	14	—	6.3
Butyl rubber	15	4.0	5.6	4.0	27	4.8
Hycar OR-15	15	2.9	4.1	5.7	22	3.4
Isoprene-acrylonitrile copolymer	15	2.3	3.7	3.3	25	2.8
Thiokol-B	3.2	—	1.2	2.4	—	—

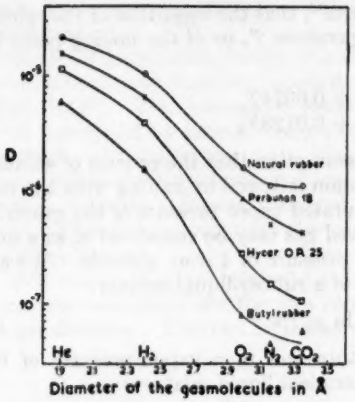


FIG. 2.—Rate of diffusion as a function of diameter of gas molecules at 25° C.

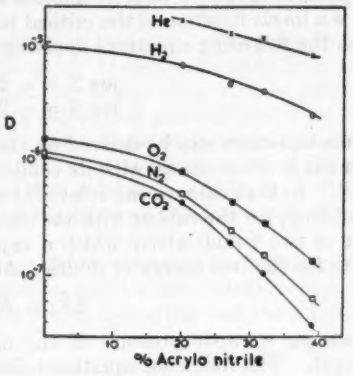


FIG. 3.—Decreasing diffusivity of butadiene-acrylonitrile copolymers with increasing nitrile content at 25° C.

Comparing Figure 3 with Figure 1, we see that in this case the permeability and diffusivity run parallel; hence apparently the solubility with respect to a certain gas is only slightly influenced by the chemical nature of the polymer. When we consider the question of the dependence of diffusivity on the temperature, we shall see why diffusivity decreases with increasing nitrile content of the polymer. As with permeability, however, the general rule applies that the presence of polar groups and of methyl groups in the polymer molecules brings about low diffusivity.

SOLUBILITY

It had been discovered in earlier experiments that the solubility of a gas is connected with its tendency to condense, of which the boiling point or the critical temperature is a measure[10]. It appears from Figure 4, which also in-

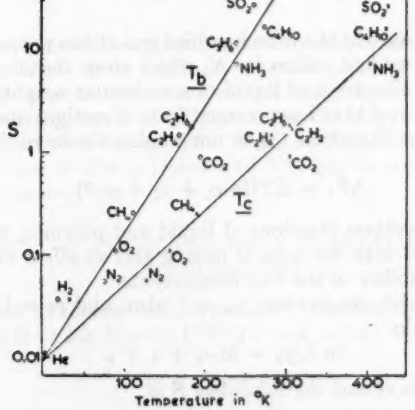


FIG. 4.—Solubility of gases in vulcanized natural rubber at 25° C as a function of critical temperature T_c and boiling point T_b.

corporates data derived from another source[10], that the logarithm of the solubility is a linear function of the critical temperature T_c or of the boiling point T_b, with the following equations applying:

$$\log S = -2.1 + 0.0074T_c$$
$$\log S = -2.1 + 0.0123T_b$$

These equations can be derived on the assumption that the process of solution of a gas is synonymous with its condensation followed by mixing with the rubber[11]. In that case we can relate the saturated vapor pressure of the gas to its solubility; for the rubber with the dissolved gas may be conceived of as a mixture of two liquids above which a vapor pressure of 1 atm. prevails. We can write for the free energy of dilution $\Delta\bar{F}_1$ of a rubber-liquid system:

$$\Delta\bar{F}_1 = RT \ln p_m/p_0 \tag{7}$$

where p_m = vapor pressure of the mixture and p_0 = vapor pressure of the solvent. The following equation holds for ideal liquid mixtures:

$$\Delta\bar{F}_1 = RT \ln N_1 \tag{8}$$

where N_1 is the molar fraction of component one in the mixture, R is the gas constant, and T is the temperature. When applying Equations (7) and (8) to the system of rubber and liquefied gas, one can take 1 atm. for p_m and the

TABLE IV

CALCULATION OF THE μ CONSTANT AT 25° C

Gas	p_0 (atm.)	V_1, cc. at 25° C	Natural rubber		German Perbunan		Butyl rubber	
			S	μ	S	μ	S	μ
N_2	1000	~50	0.055	~1.1	0.032	~1.6	0.055	~1.1
O_2	700	~50	0.112	~0.7	0.068	~1.2	0.122	~0.65
CH_4	370	~50	0.25	~0.55				
CO_2	63.5	63	0.90	0.8	1.24	0.5	0.68	1.1
C_2H_2	47	68	1.62	0.45	2.48	0.05	0.63	1.4
C_2H_6	9.5	89	6.5	0.4				
C_4H_{10}	2.6	101	16	0.65				
NH_3	9.9	28.4	6.9	1.45	13.5	0.75	~1.2	~3.2
SO_2	3.8	49	23.6	0.6	48	−0.1	~3.6	~2.5

saturated vapor pressure of the pure liquefied gas at the prevailing temperature for p_0. In so doing we find values for N_1 which show that in this case the rubber seems to behave like an ideal liquid of a molecular weight of approximately 300. A well-known fact that has emerged from investigations respecting swelling, however, is that Equation (8) is not applicable to rubber. In its stead Huggins[12] found:

$$\Delta\bar{F}_1 = RT(\ln v_1 + v_2 + \mu v_2^2) \tag{9}$$

where v_1 and v_2 are volume fractions of liquid and polymer, respectively. μ is a constant connected with the heat of mixing and an effect of entropy, and related to the compatibility of the two components.

Assuming that with gas-rubber, p_m = 1 atm. and v_2 = 1, then combining (7) and (9), we obtain:

$$\ln 1/p_0 = \ln v_1 + 1 + \mu \tag{10}$$

The relation between v_1 and the solubility S is:

$$v_1 = SV_1/22{,}400 \tag{11}$$

where V_1 is the molar volume of the liquefied gas at the temperature of the experiment.

Table IV gives some results of μ calculated in this way. The pressure and the molecular volume of the liquefied gases at 25° C were calculated from published data[13]. The pressure of gases which are above their critical point at 25° C was found by extrapolating to above the critical point of the ln p_0: $1/T$ function[14]. At the boiling point, the molecular volume of these gases is 30 to 40 cc., and it increases with the temperature. The assumed value of 50 cc. is a rough estimate. It was supposed that the solubility of NH_3 and SO_2 in Butyl rubber is approximately the same as the known solubility of these gases in polyisobutene[3].

It is known that μ is below 0.5 for compatible systems, so the higher μ is, so much less compatible are the two components, and the less satisfactorily does the gas dissolve. This can be stated more simply by saying that the solubility

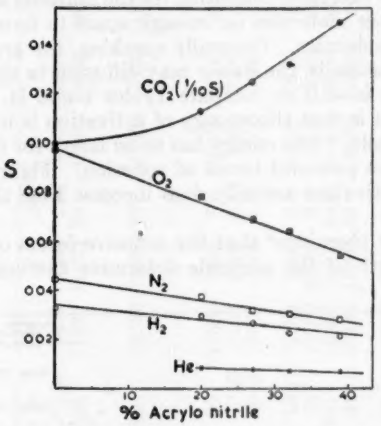


FIG. 5.—Gas solubility in butadiene-acrylonitrile copolymers at 25° C.

of a given gas in various rubbers is influenced by a specific interaction between the gas and the rubber. As a result, a nonpolar gas, like H_2 or O_2, dissolves rather more readily in a nonpolar rubber than in a polar one. Gases of a polar nature, on the contrary, such as CO_2 or NH_3, dissolve more readily if more polar groups are present in the rubber. Figure 5 illustrates this reciprocal influence of the nature of the polymer and the gas in a series of butadiene-acrylonitrile copolymers.

DEPENDENCE OF PERMEABILITY AND DIFFUSIVITY UPON TEMPERATURE

On the evidence of former measurements[15], when a linear connection was found between log Q or log D with $1/T$, we may write:

$$Q = Q_0 e^{-W/RT} \tag{12}$$

$$D = D_0 e^{-E/RT} \tag{13}$$

where Q_0 and D_0 are constants, W is the activation energy for the permeation, and E is the activation energy for the diffusion.

We shall see presently that the assumption of a linear connection of log Q or log D with $1/T$ is tenable only within a very limited range of temperature and that the activation energies depend on the temperature. At a first approximation, Equations (12) and (13) may be applied to the 25° C range, up to which the measurements in Table II extend, and it is permissible to regard the energies as being constant. The various energies thus calculated are presented in Table V.

The energy of activation for the permeation is of little theoretical value, and is used only for the calculation of the heat of solution.

ENERGY OF ACTIVATION FOR DIFFUSION

RELATION TO ENERGY OF COHESION

We may define the energy of activation for the diffusion as the energy necessary to push the rubber molecules far enough apart to form a hole for the infiltration of the gas molecules. Generally speaking, the greater the energy of activation for the diffusion is, the slower may diffusion be expected to be. We find that this actually is so if we compare Tables V and II.

Another prediction is that this energy of activation is in proportion to the necessary size of the hole. The energy has to be larger for the larger gas molecules and for the more powerful forces of cohesion. Figure 6 makes it plain that the energy of activation actually does increase with the diameter of the gas molecules.

It was pointed out elsewhere[3] that the cohesive forces of the rubber molecules per unit of length of the molecule determine the energy of activation.

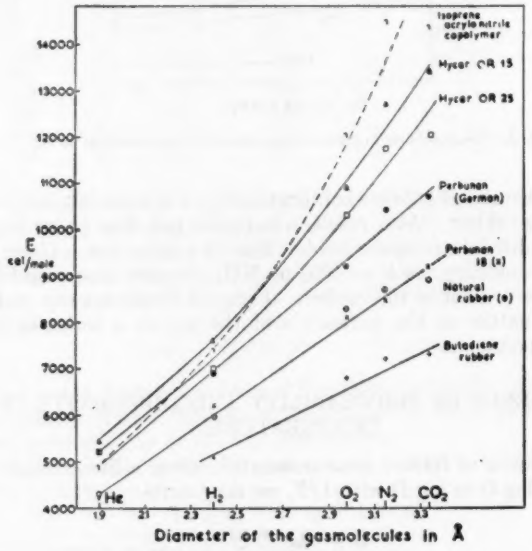


FIG. 6.—Relationship between energy of activation and diameter of the gas molecules.

TABLE V

ENERGIES OF ACTIVATION (CAL./MOLE) W AND E FOR PERMEATION AND DIFFUSION WITH THE CONSTANTS D_0 AT 25–50° C

Compound	H_2			N_2			O_2			CO_2			He			C_2H_2		
	W	E	D_0	W	E	D_0	W	E	D_0	W	E	D_0	W	E	D_0	W	E	D_0
Natural rubber	6800	6000	0.26	8800	8700	2.6	7500	8300	1.94	6100	8900	3.7	6100	4300	0.031	7300	9500	4.3
Methyl rubber	8000	7500	1.3	13300	12400	105	11300	11100	20	11200	12800	160	6600					
Isoprene-acrylonitrile copolymer	9100	7400	0.67	15000	14500	1880	12700	12100	70	12500	14400	1150	7600	4900	0.031			
Isoprene-methacrylonitrile copolymer	8100	6900	0.41	12800	11600	39	11000	9600	2.6	10100	12200	81						
Polybutadiene	6600	5100	0.053	8200	7200	0.22	7100	6800	0.15	5200	7300	0.24						
Perbunan-18	7200	6200	0.23	9900	8500	0.88	8600	8100	0.69	7000	9200	2.4	6800	4200	0.019			
Perbunan (German)	7900	6900	0.52	11400	10400	10.7	9700	9200	2.4	8100	10700	13.5	7000	5200	0.077	9800	12300	82
Hycar OR-25	8200	7000	0.52	12300	11700	56	10500	10300	9.9	9000	12000	67	7400	5200	0.074			
Hycar OR-15	8800	7600	0.92	13800	12700	131	12000	10900	13.6	10500	13400	260	7700	5500	0.087			
Butyl rubber	8700	8100	1.36	12500	12100	34	10700	11900	43	9900	12000	36	7600	5800	0.105	11600	12800	50
Polymethyl-pentadiene	7100	—	—	11200	11100	42	9400	9800	8.5	8300	—	—						
Vulcaprene-A	9000	7600	0.98	12200	11700	55	10900	10200	7.5	9400	11800	42						

Greater energy is needed if a larger number of polar and methyl groups is present in the polymer molecules. This effect of polar groups in the polymer on the energy of activation is very clearly exemplified in the series of butadiene-acrylonitrile copolymers, for which see Figure 7.

From Figure 8 it can be deduced how methyl groups in the rubber increase the energy of activation. This increase runs entirely parallel with the energy of cohesion of a monomeric unit, as a measure of which the boiling point of the monomer was taken on the assumption that Trouton's rule applies. Thus methyl groups not only raise the boiling point and increase the energy of cohesion of the monomer, but also the energy of cohesion per unit of chain length and the energy of activation in the polymer.

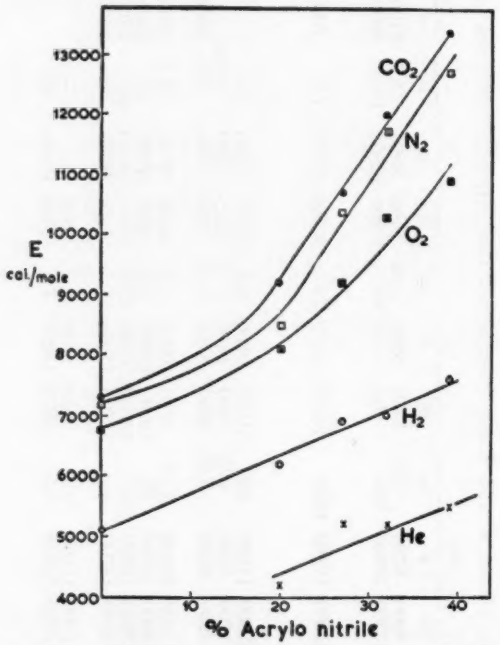


FIG. 7.—Influence of the nitrile content on the energy of activation for diffusion in the case of butadiene-acrylonitrile copolymers.

It is necessary to stress at this point that the cohesive energy per unit of length of the macromolecule, which may be considered as determining the activation energy, is distinct from the cohesive energy density (C.E.D), this latter, giving the cohesive energy per cubic centimeter of material. It will be evident that there are far fewer monomeric units per cubic centimeter in methyl rubber than in butadiene rubber; quite possibly, therefore, there may be little difference between the C.E.D. values of these two rubbers, even if there is considerable difference in the cohesive energy of a unit of length of the macromolecules. The discovery made by Barrer and Skirrow[16], *viz.*, that, according to gas solubility measurements, the C.E.D. of a series of rubber-sulfur vulcanizates remains

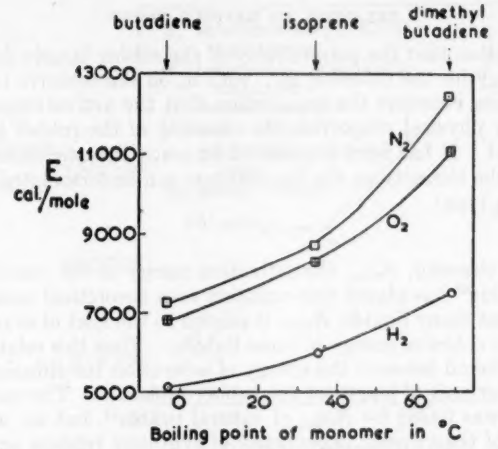


FIG. 8.—Relation of boiling point of dienes to energy of activation for the diffusion in their polymers.

virtually unchanged with increasing sulfur content, does not necessarily imply that the cohesive energy per unit length of the chain molecule remains unchanged. It is arguable that the introduction of combined sulfur causes a reduction in the total length of the chain per cubic centimeter of material, because the combined sulfur does not contribute to the length of the chain, and the density of the rubber does not increase in proportion to the quantity of combined sulfur. Moreover, the binding of the sulfur is probably accompanied by considerable shortening of the chains through cyclization, which, with unchanged C.E.D., is responsible for further increase in the calculated cohesive energy per unit of chain length. In point of fact[17], an increase in the combined sulfur content from 1.7 to 11.3 per cent does go hand in hand with an increase in the activation energy for N_2 from 8000 to 11,000 cal. per mole.

To obtain a rubber with a high activation energy and, with it, a low rate of diffusion and permeability, it seemed obvious that methyl groups should be combined with strongly polar groups. And the argument was vindicated by copolymers of isoprene with acrylonitrile and methacrylonitrile, which combine rubberlike properties with an exceptionally marked activation energy together with very low permeability superior to most of the other varieties of rubber.

Table VI shows how much lower is the permeability and greater the activation energy of isoprene copolymers than of butadiene copolymers of the same nitrile content. The values for the butadiene copolymers were estimated from Figures 1 and 7.

TABLE VI

ISOPRENE COPOLYMERS COMPARED WITH BUTADIENE COPOLYMERS AT 25° C

Compound	% N	Q_{H_2}	Q_{N_2}	E_{H_2}	E_{N_2}
Isoprene-acrylonitrile	7.0	5.7	0.14	7400	14,500
Butadiene-acrylonitrile	7.0	12.5	0.85	6700	10,100
Isoprene-methacrylonitrile	5.3	10.4	0.46	6900	11,600
Butadiene-acrylonitrile	5.3	19	1.9	6200	8,500

RELATION TO BRITTLE POINT

The assumption that the permeability of the rubber largely depends on the activation energy for the diffusion and, with it, on the cohesive forces between the rubber chains connotes the supposition that the activation energy can be related to other physical properties, the viscosity of the rubber being the first to come to mind. It has been established by many investigations that the dependence of the viscosity on the temperature can be formulated by equations of the following type:

$$\eta = Ae^{E_{visc.}/RT} \tag{14}$$

where η is the viscosity, $E_{visc.}$ the activation energy of the viscosity, and A a constant. Eyring[18] has placed this equation on a theoretical basis. He found that, with a great many liquids, $E_{visc.}$ is related to the heat of evaporation and, therefore, to the cohesive energy of those liquids. Thus this relation resembles the connection found between the energy of activation for diffusion and the cohesive energy per unit of length of the rubber molecule. The value of 8 to 10 kcal. per mole was found for $E_{visc.}$ of natural rubber[19], but as, unfortunately, measurements of the vicosity dependence of synthetic rubbers on temperature are not yet available, no further comparison with the activation energy for diffusion is possible.

The brittle point[20] is another important quantity to which the activation energy for diffusion can be related. As a rubberlike material cools down, its rubberlike properties gradually disappear; it becomes harder and harder, until ultimately it will break or disintegrate under a sudden impact of force. The temperature at which such fracture occurs is known as the brittle point. This point serves as an index as to the utilizability of rubber at low temperatures. The brittle point test has to be performed under standardized conditions, because the position of the point depends to some extent on the force to which the material is subjected. Fracture occurs the moment the material ceases, within the time allowed, to give way by deformation to the force applied.

The total deformation D of a viscoelastic material may consist of a high-elastic and a viscous-plastic component[21].

$$D = D_{h.e.} + D_{visc.} \tag{15}$$

This can be reduced to:

$$D = D_{h.e.(\infty)}[1 - e^{-t/\tau}] + \sigma t/\eta \tag{16}$$

where D is the total deformation, $D_{h.e.(\infty)}$ is high-elastic deformation after infinite time, σ is the stress, η is the viscosity coefficient, τ is the orientation time, and t is the time.

Both the orientation time τ and the viscosity η can be related to an activation energy by equations such as (14), from which it follows that, the higher the activation energies, the higher are τ and η and the lower is the amount of deformation under a given force within a given time, this being manifested by increasing brittleness of the material. Since in the brittle point test the amount of deformation is kept constant while the temperature is varied, greater activation energy results in a higher brittle point temperature. The assumption that greater activation energy for diffusion is related to greater activation energy for the viscosity leads to the conclusion that rubber with a high activation energy for diffusion must possess a high brittle point; and that experiment has shown this to be so is evident from Figure 9.

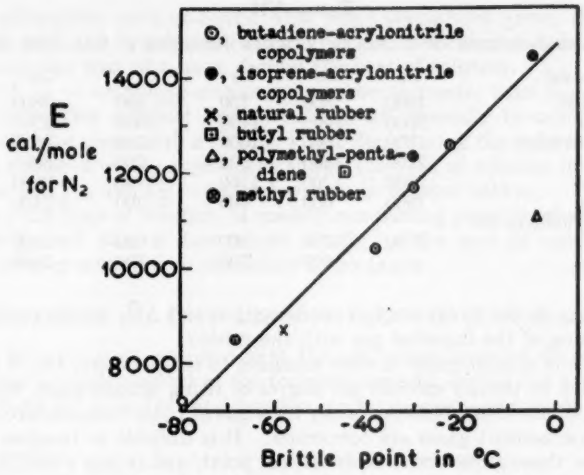


FIG. 9.—Relationship between the activation energy for the diffusion of nitrogen and the brittle point in some elastomers.

The brittle points cited have been borrowed from measurements performed by Salomon[22] and by Boonstra[23]. The correlation is clearly evident on the whole, the exceptions being that Butyl rubber has greater activation energy than the position of the brittle point would lead one to expect, whereas polymethylpentadiene exhibits insufficient activation energy, possibly due to the very irregular buildup of this polymer.

HEAT OF SOLUTION

We can calculate the heat of solution of the gas in the elastomer from the dependency of the permeation and diffusion on the temperature by substitution of Equations (12) and (13) in the basic equation $Q = DS$, which gives:

$$S = S_0 e^{-\Delta H/RT} \tag{17}$$

and:

$$\Delta H = W - E \tag{18}$$

where $S_0 = Q_0/D_0$ is a constant and ΔH is the heat of solution. In a previous publication[3] the heat of solution was expressed somewhat differently as $H = \Delta H + RT$ cal. per mole, where, therefore, the figures are +600 cal. per mole higher.

Table VII sets out the heats of solution now found. These figures are accurate to within about 400 cal. per mole. A fact to be noted is that the gases which do not readily condense generally exhibit heat absorption, which is compatible with the fact that the solubility of these gases increases a little with the temperature.

We may represent the process of solution of a gas as consisting in condensation of the gas combined with the mixing of that condensed gas with the rubber[24]. As a result, the heat of solution subdivides as follows:

$$\Delta H = \Delta H_{cond.} + \Delta \bar{H}_1 \tag{19}$$

TABLE VII

HEATS OF SOLUTION OF GASES IN VARIOUS RUBBERS IN CAL. PER MOLE

Compound	He	H_2	N_2	O_2	CO_2	C_2H_2
Natural rubber	1800	800	100	− 800	−2800	−2200
Perbunan-18	2600	1000	1400	500	−2200	
Perbunan (German)	1800	1000	1000	500	−2600	−2500
Hycar OR-25	2200	1200	600	200	−3000	
Hycar OR-15	2200	1200	1100	1100	−2900	
Butyl rubber	1800	600	400	−1200	−2100	−1200
Isoprene-acrylonitrile copolymer	2700	1700	500	600	−1900	
Vulcaprene-A		1400	500	700	−2400	

where $\Delta H_{cond.}$ is the molar heat of condensation and $\Delta \bar{H}_1$, is the partial molar heat of mixing of the liquefied gas with the rubber.

The heat of condensation is very sensitive to temperature, *i.e.*, it decreases by about five to twenty calories per degree of rising temperature, which often makes it difficult to establish it exactly for a gas at room temperature, certainly where the permanent gases are concerned. It is difficult to imagine any condensation of these gases above their critical point, and in any event it does not readily lend itself to calculation of the heat of condensation. It can, however, be positively asserted that this "heat of condensation" of gases such as He, H_2 N_2 and O_2 is very low at room temperature, since the heat of evaporation at the boiling point of these gases is very low, *viz.*, 24, 216, 1360, and 1610 cal. per mole, respectively. Furthermore, owing to the dependence on temperature and the great temperature difference between the boiling point and room temperature, these figures should be a good deal lower still at room temperature. Therefore, so far as He and H_2 are concerned, there is no necessity to take considerable (negative) heat of condensation into account. In these cases the heat of solution is determined chiefly by the heat of mixing, which can be calculated by means of Hildebrand's equation[25]:

$$\Delta \bar{H}_1 = V_1[(E_1/V_1)^{\frac{1}{2}} - (E_2/V_2)^{\frac{1}{2}}]^2 v_2^2 \qquad (20)$$

and also according to [12]:

$$\Delta \bar{H}_1 = (RT/v_2^2)[\mu - 1/z] \qquad (21)$$

where V_1 and V_2 = molar volume of the liquefied gas and the rubber, respectively; E_1 and E_2 = energy of vaporization of the liquefied gas and the rubber, respectively; E_1/V_1 and E_2/V_2 = cohesion energy density (C.E.D.) of the liquefied gas and the rubber, respectively; v_2 = volume fraction of rubber ($\simeq$1 in this case); z = coördination number (usually $z \simeq 6$ to 8); and μ = a constant given by Equation (9).

If we apply these equations to the permanent gases, we are again faced with the difficulty that the cohesion energy density (C.E.D.) cannot be calculated for these gases at room temperature. At the boiling point of He, H_2, N_2, and O_2, however, $(E_1/V_1)^{\frac{1}{2}}$ amounts to 0.67, 2.5, 5.9, and 7.4, respectively, but it decreases in a marked degree with rising temperature, owing to decreasing E_1 and increasing V_1. If these excessive C.E.D. values are used for the calculation of the heat of mixing with natural rubber[26] $[(E_2/V_2)^{\frac{1}{2}} = 7.98]$, the results are 1800, 900, 140, and 10 cal. per mole, respectively, which may presumably be higher.

The heat of mixing can also be calculated with the aid of Equation (21), using the value for μ given in Table IV. Here again the result is a positive value for the heat of mixing.

Heat absorption such as found with some permanent gases, therefore, is compatible with the hypothesis that the heat of condensation is low and that consequently the heat of mixing decides the heat of solution.

The C.E.D. of butadiene-acrylonitrile rubber is greater than that of natural rubber. From this a higher heat of mixing can generally be calculated from Equation (20) for gases with a C.E.D. lower than that of the rubber. Accordingly, the evidence of the experiment shows the heat of solution in these rubbers of He, H_2, N_2, and O_2 to be higher than in natural rubber.

Finally, the heat of solution of readily condensing gases, such as propane, butane, NH_3, and SO_2, is determined chiefly by the heat of condensation[11], while the heat of mixing is of secondary importance.

DEPENDENCE OF ACTIVATION ENERGY ON TEMPERATURE

It has hitherto been assumed that the activation energies for permeation and diffusion are independent of the temperature and, within the experimental range of 25 to 50° C under consideration, this approximately meets the facts.

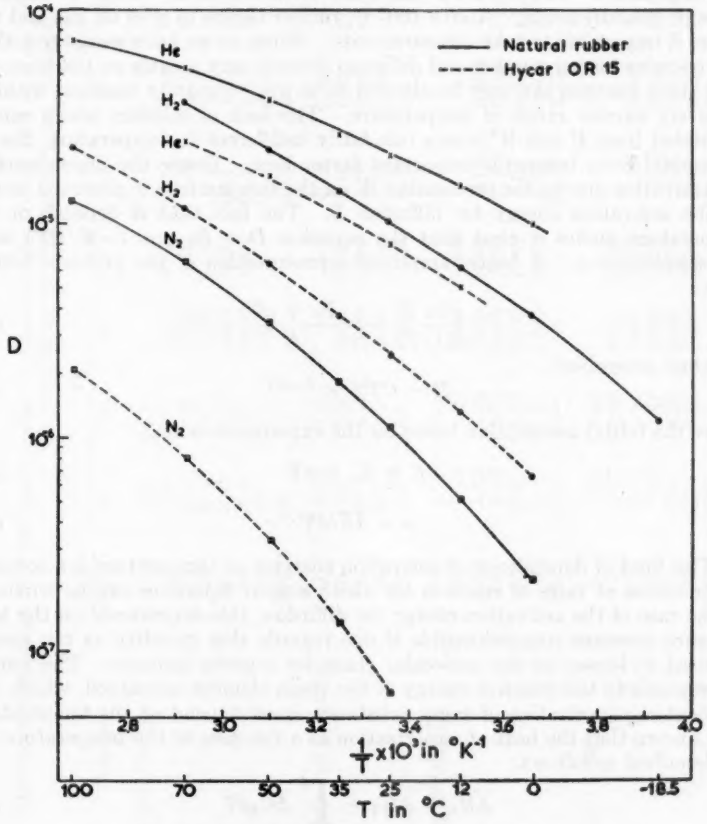


FIG. 10.—Rate of diffusion as a function of temperature.

There were grounds, however, for questioning the validity of this assumption as applied to a wider range of temperature and measurements were, therefore, performed on a few gases and rubbers at temperatures ranging from −18.5 to +100° C.

Figure 10 shows that the relation between log D and $1/T$ within a wider range of temperature is no longer linear, despite the first impression that it is. At the higher temperatures D is lower than it should be if the relation were truly linear. A similar curvature is obtained when log Q is plotted against $1/T$. Barrer and Skirrow[17] find a similar response of D and Q to the temperature in the majority of the cases they investigated.

The changing slope of the log D:$1/T$ and log Q:$1/T$ curves can be interpreted as a change in the activation energies for diffusion and permeation caused by changing temperature. The permeabilities, diffusivities, and activation energies within the measured temperature limits are set out in Table VIII.

Generally speaking, measurements within so wide a temperature range are less precise than at normal temperature. One difficulty is that the measurements at all these temperatures cannot be performed with a membrane of the same thickness. The reported values are often the result of two overlapping series of measurements. Above 100° C, rubber begins to give off gas and this makes it impossible to take measurements. Since, as we have seen, the activation energies for permeation and diffusion depend very greatly on the temperature, these energies can only be allowed to be approximately constant within a relatively narrow range of temperature. The heat of solution which can be calculated from E and W is as a rule fairly indifferent to temperature, the experimental error being the important factor here. Hence the dependence of the activation energy for permeation W on the temperature is governed chiefly by the activation energy for diffusion E. The fact that E depends on the temperature makes it clear that the equation $D = D_0$ exp. $(-E/RT)$ is an oversimplification. A better empirical representation of the problem follows from:

$$\frac{d \ln D}{d(1/T)} = -\frac{E_0 + aT}{R} \tag{22}$$

or, when integrated:

$$D = CT^{a/R}e^{-E_0/RT} \tag{23}$$

where the initial assumption based on the experiment is that:

$$E = E_0 + aT \tag{24}$$

and:

$$a = dE/dT \tag{25}$$

This kind of dependence of activation energies on temperature is a common phenomenon at rates of reaction for which similar equations can be written[27]. In the case of the activation energy for diffusion, this dependence on the temperature becomes comprehensible if one regards this quantity as the energy required to loosen up the molecular chain for a given distance. This energy corresponds to the cohesive energy of the chain element concerned, which, like the heat of vaporization of every substance, must depend on the temperature. It is known that the heat of vaporization as a function of the temperature can be described as follows:

$$\Delta H_v = \Delta H_0 + \int_0^T \Delta C_p dT \tag{26}$$

TABLE VIII

PERMEABILITIES Q (IN 10^{-8} CM.^{2} SEC.$^{-1}$ ATM.$^{-1}$), DIFFUSIVITIES D (IN 10^{-6} CM.^{2} SEC.$^{-1}$) AND ENERGIES OF ACTIVATION W AND E (IN CAL./MOLE) IN DEPENDENCY ON TEMPERATURE

Compound	Temp. (° C)	H_2				N_2				He			
		Q	D	W	E	Q	D	W	E	Q	D	W	E
Natural rubber	− 18.5	3.8	1.3										
	0	11.9	3.7	8100	7100	1.14	0.22	—	—	8.5	10.0		
	12	21.5	6.2	7600	6700	2.80	0.52	11,110	10,700	14.6	15.0	6800	5100
	25	37.4	10.2	7100	6300	6.12	1.10	9,700	9,400	23.7	21.6	6300	4700
	35	55.0	14.2	6800	6000	10.2	1.82	8,900	8,800	33.3	27.7	6100	4400
	50	90.8	22.2	6400	5800	19.4	3.42	8,100	7,900	52.3	38,0	5900	4000
	70	157	37.1	5800	—	39.0	6.63	7,000	6,600	88.8	53.4	5700	3300
	100	298	—	—	—	80.3	13.0	—	—	170.5	72.1		
Perbunan (German)	12	6.35	2.53	—	—	0.31	0.105	—	—				
	25	12.1	4.50	8200	7400	0.81	0.25	12,200	11,200				
	35	18.7	6.70	7900	7000	1.56	0.46	11,500	10,600				
	50	33.7	11.1	7600	6300	3.58	0.98	10,500	8,300				
	70	64.8	18.9	7000	5000	8.79	2.1	9,500	—				
Hycar OR-15	0	1.22	0.665										
	12	2.63	1.32	9900	8600	—	—	—	—	2.81	5.00	—	—
	25	5.42	2.43	9200	8000	0.179	0.064	—	—	5.20	7.92	7900	5800
	35	8.90	3.74	8800	7700	0.400	0.138	13,900	13,100	8.00	10.7	7700	5500
	50	17.0	6.56	8300	7100	1.08	0.338	12,900	10,900	14.2	16.2	7400	5000
	70	34.7	11.9	7500	6200	3.40	0.805	11,600	9,000	27.4	24.2	—	—
	100	80.2	23.0	—	—	11.50	2.12						
Butyl rubber	0	1.26	0.41										
	12	2.77	0.80	9800	8700	—	—	—	—	3.6	3.7	—	—
	25	5.50	1.52	9000	8400	0.25	0.045	—	—	6.4	5.9	7600	6100
	35	9.00	2.41	8800	8200	0.50	0.090	12,600	12,200	9.8	8.3	7600	5800
	50	17.2	4.38	8600	7500	1.27	0.22	11,800	11,400	17.3	12.6	7500	5400
	70	37.0	8.24	8200	6800	3.53	0.59	11,100	10,000	33.7	20.0	—	—
	100	91.8	17.6	—	—	13.1	1.7	—	—				

TABLE IX

dE/dT VALUES FOR SOME DIFFUSIONS

Compound	H_2	N_2	He
Natural rubber	−28	− 68	−32
Perbunan (German)	−52	− 80	—
Hycar OR-15	−42	−114	−32
Butyl rubber	−33	− 66	−28

where ΔH_v is the heat of vaporization, ΔH_0 is a constant, and ΔC_p is change in specific heat on vaporization. Assuming ΔC_p to be a constant, we get an equation similar to (24) after integration.

Table IX gives the values for dE/dT obtained from the smoothed linear curve $E:T$.

THEORETICAL DISCUSSION

It will be interesting to see whether dependence of E on the temperature can be made to fit into the zone theory propounded by Barrer[28] and the transition state theory developed by Eyring[18] to account for the process of diffusion.

Certainly, the zone theory does require E to be a function of the temperature. According to this theory, diffusion answers the equation:

$$D = \tfrac{1}{6}\nu d^2 e^{-E_0/RT} \sum_{f=1}^{n} \left(\frac{E_0}{RT}\right)^{f-1} \frac{1}{(f-1)!} \qquad (27)$$

where ν is frequency, d is distance, E_0 is total energy of activation, and f is number of degrees of freedom for activation. If we suppose that the first term of the series is the decisive factor, it can be deduced[29] that:

$$E = E_0 - (f-1)RT \qquad (28)$$

and:

$$dE/dT = -(f-1)R \qquad (29)$$

Then, with the aid of Equation (29), we can find directly from Table IX the number of degrees of freedom which, according to the zone theory, have to be reckoned with for the activation in the process of diffusion.

An alternative is to apply the transition theory[18] to diffusion. This theory starts from the assumption that diffusion is a reaction satisfying the following equation:

$$\mathrm{D} = d^2 k^1 \qquad (30)$$

where d is the jump and distance k^1 is a rate constant.

The constant k^1 follows from:

$$k^1 = \kappa(kT/h)K^{\ddagger} \qquad (31)$$

where k is the Boltzmann constant, h is the Planck constant, κ is the transmission coefficient (usually $\kappa \simeq 1$), and $K^{\ddagger}$ is the equilibrium constant for activated and initial states.

It is supposed here that diffusion takes place after an activated state has been reached which is in equilibrium with the initial state. The constant $K^{\ddagger}$ stands in relation to the standard free energy of the process by means of the familiar thermodynamic equation:

$$\ln K^{\ddagger} = -\Delta F^{\ddagger}/RT \qquad (32)$$

Also:

$$\Delta F^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} \tag{33}$$

where $\Delta F^{\ddagger}$, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ are the standard free energy, heat, and entropy changes, respectively.

After substitution of (33) in (32) and thereafter of (32) in (31) and (30). we obtain:

$$D = \kappa(kT/h)d^2 e^{\Delta S^{\ddagger}/R} e^{-\Delta H^{\ddagger}/RT} \tag{34}$$

This equation agrees with Equation (13) found by experiment, where:

$$E = \Delta H^{\ddagger} + RT \tag{35}$$

and:

$$D_0 = \frac{\kappa k T d^2}{he} e^{\Delta S^{\ddagger}/R} \tag{36}$$

If $\Delta S^{\ddagger}$ is calculated according to Equation (36), we find values of 10 to 26 entropy units per mole[17].

If it be desired to apply Equation (34) to a diffusion process, where the activation energy is dependent on temperature, the proper course would seem to be to take the dependence of $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ on the temperature also into account. For this we can write:

$$\Delta H^{\ddagger} = \Delta H^{\ddagger}_0 + \int_0^T \Delta C^{\ddagger}_p dT \tag{37}$$

and:

$$\Delta S^{\ddagger} = \Delta S^{\ddagger}_0 + \int_0^T (\Delta C^{\ddagger}_p/T)\, dT \tag{38}$$

where $\Delta H^{\ddagger}_0$ and $\Delta S^{\ddagger}_0$ are constants and $\Delta C^{\ddagger}_p$ is change in specific heat on activation. After substitution of (37) and (38) in (33) and (32), we obtain:

$$\ln K^{\ddagger} = -\frac{\Delta H^{\ddagger}_0}{RT} + \frac{S^{\ddagger}_0}{R} - \frac{1}{RT}\left\{\int_0^T \Delta C^{\ddagger}_p dT - T\int_0^T \frac{\Delta C^{\ddagger}_p}{T} dT\right\} \tag{39}$$

For $\Delta C^{\ddagger}_p$ we can write:

$$\Delta C^{\ddagger}_p = \alpha + \beta T + \gamma T^2 + \ldots \tag{40}$$

Considering only the first two terms, we get from this:

$$\ln K^{\ddagger} = -\frac{\Delta H^{\ddagger}_0}{RT} + \frac{\Delta S^{\ddagger}_0}{R} - \frac{\alpha}{R} + \frac{\alpha \ln T}{R} + \frac{\beta T}{2R} \tag{41}$$

In (31) and (30) this gives:

$$D = \kappa \frac{kT}{h} e^{(\Delta S^{\ddagger}_0 - \alpha + \frac{1}{2}\beta T)/R}\, T^{\alpha/R}\, e^{-\Delta H^{\ddagger}_0/RT} \tag{42}$$

The formal agreement between this equation and Equation (23), which was found experimentally, is satisfactory.

From (13 and (42) one finds the following for the dependence of the energy of activation on the temperature:

$$\frac{d \ln D}{d(1/T)} = -\frac{E}{R} = -\frac{\Delta H^{\ddagger}_0}{R} - \frac{\alpha T}{R} - \frac{\beta T^2}{2R} - T \tag{43}$$

or:

$$E = \Delta H_0 + (\alpha + R)T + \tfrac{1}{2}\beta T^2 \qquad (44)$$

which, after disregarding the β term, is likewise the dependence on temperature found experimentally, where $dE/dT = \alpha + R$. It should be noted that the constants $\Delta H^{\ddagger}_0$ and $\Delta S^{\ddagger}_0$ are only of account insofar as they are used within the measuring range in Equation (42), because only two terms of the progression of $\Delta C^{\ddagger}_p$ were used.

THE CONSTANT D_0

We see in Table V that the constant D_0 is larger in proportion to the greater energy of activation E. It has been shown before[3] how the two quantities stand in relation to each other, regardless of the diffusion process, approximately according to:

$$\log D_0 = E/2000 - 4.2 \qquad (45)$$

A comparable functional relationship was found by Barrer and Skirrow[17], who also suggest possible interpretations of the constant D_0 on the basis of the transition state theory[18] and the zone theory[30].

It is obvious that there must be some close connection between this relation ship and the fact that the activation energy E is a function of the temperature. And, in fact, D_0 is not constant for the diffusion of a given gas through rubber, but also depends upon the temperature, according to:

$$D_0 = C(Te)^{a/R} \qquad (46)$$

which equation can be derived from (23). A complete interpretation of D_0 should bring Equation (45) into relation with Equation (46).

ACKNOWLEDGMENTS

In conclusion, I wish to express my sincere thanks to Miss W. Karssen for her able assistance in carrying out the experiments, to Dr. G. Salomon for his interest and discussions, and to the Rubber Foundation for permission to publish the results of the investigation.

REFERENCES

[1] Barrer, *Trans. Faraday Soc.* **35**, 628 (1939); Sager, *J. Research Natl. Bur. Standards* **25**, 309 (1940); van Amerongen, *Rev. gén. caoutchouc* **21**, 50 (1944); RUBBER CHEM. & TECHNOL. **20**, 479 (1947); *J. Applied Physics* **17**, 972 (1946); RUBBER CHEM. & TECHNOL. **20**, 495 (1947); Barrow and Skirrow, *J. Polymer Sci.* **3**, 549, 564 (1948).
[2] Van Amerongen, *J. Applied Physics* **17**, 972 (1946); RUBBER CHEM. & TECHNOL. **20**, 495, (1947); *J. Polymer Sci.* **2**, 381 (1947).
[3] Van Amerongen, *J. Applied Physics* **17**, 972 (1946); RUBBER CHEM. & TECHNOL. **20**, 495 (1947).
[4] McMillan, Bishop, Marple, and Evans, *India Rubber World* **113**, 663 (1946).
[5] Acknowledgments are due W. Gaade and G. Salomon for their kindness in carrying out these polymerizations.
[6] The helium gas came from Philips Co., and was generously placed at our disposal by the Kamerlingh Onnes Laboratory of Leyden, Holland.
[7] Sager, *J. Research Natl. Bur. Standards* **25**, 309 (1940); Barrow and Skirrow, *J. Polymer Sci.* **3**, 549 (1948).
[8] Carpenter, *Trans. Faraday Soc.* **43**, 529, 822 (1947).
[9] Hodgman, "Handbook of Chemistry and Physics," Cleveland, 29th Ed., **1945**.
[10] Van Amerongen, *J. Applied Physics* **17**, 972 (1946); RUBBER CHEM. & TECHNOL. **20**, 495 (1947); Barrer and Skirrow, *J. Polymer Sci.* **3**, 564 (1948).
[11] Gee, *Quart. Revs.* (London) **1**, 295 (1947); RUBBER CHEM. & TECHNOL. **21**, 591 (1948); Barrer and Skirrow, *J. Polymer Sci.* **3**, 564 (1948).
[12] Huggins, *Ann. N. Y. Acad. Sci.* **43**, 1 (1942); **44**, 431 (1943).
[13] Landolt-Bornstein, "Physikalisch-Chemische Tabellen," Springer, Berlin, **1923-1936**; Hodgman, "Handbook of Chemistry and Physics," Cleveland, 29th Ed., **1945**.
[14] Hildebrand, "Solubility," New York, **1936**, p. 30.
[15] Barrer, *Trans. Faraday Soc.* **35**, 628 (1939); van Amerongen, *J. Applied Physics* **17**, 972 (1946); RUBBER CHEM. & TECHNOL. **20**, 495 (1947).
[16] Barrer and Skirrow, *J. Polymer Sci.* **3**, 564 (1948).
[17] Barrer and Skirrow, *J. Polymer Sci.* **3**, 549 (1948).

[18] Glasstone, Laidler, and Eyring, "Theory of Rate Processes," New York, 1941, p. 516.
[19] Smallwood, *J. Applied Physics* **8**, 505 (1937); Saunders and Treloar, *Trans. Inst. Rubber Ind.* **24**, 92 (1948).
[20] Boyer and Spencer, in "Advances in Colloid Science," edited by Mark and Whitby, New York, 1946, Vol. 2, p. 35.
[21] Tuckett, *Trans. Faraday Soc.* **39**, 158 (1943).
[22] Salomon and Koningsberger, *J. Polymer Sci.* **2**, 522 (1947); Salomon, *J. Polymer Sci.* **3**, 22 (1948).
[23] Boonstra, unpublished measurements.
[24] Gee, *Quart. Revs.* (London) **1**, 295 (1947); RUBBER CHEM. & TECHNOL. **21**, 591 (1948).
[25] Hildebrand, "Solubility," New York, 1936, p. 73.
[26] Gee, in "Advances in Colloid Science," edited by Mark and Whitby, New York, 1946, Vol. 2, p. 186.
[27] Moelwyn-Hughes, "Reactions in Solution," Oxford, 2nd Ed., 1947, pp. 4, 53.
[28] Barrer, *Trans. Faraday Soc.* **38**, 322 (1942); **39**, 237 (1943).
[29] Barrer, *Trans. Faraday Soc.* **39**, 237 (1943).
[30] Barrer, *Trans. Faraday Soc.* **38**, 322 (1942).

EQUATION OF STATE OF RUBBER FROM THE VIEWPOINT OF THERMODYNAMICS *

G. M. BARTENEV

MOSCOW INSTITUTE OF FINE CHEMICAL TECHNOLOGY, CHAIR OF RUBBER CHEMISTRY AND PHYSICS

By the "equation of state of rubber" is usually meant, although not absolutely accurately, the following thermodynamic relation:

$$F = F(p, T, L) \text{ or } F = F(V, T, L)$$

in which F is the applied extension or compressive force; p the external pressure, V the volume of the test-specimen, T the absolute temperature, and L the length of the elongated or compressed specimen.

There are two ways of deriving the above equation, *i.e.*, the thermodynamic and the molecular kinetic method. The first method indicates only in a general way the equation of state. However, even with this incomplete information, very important conclusions can be drawn. The other method, the molecular-kinetic, shows certain concrete functional relations.

Although this problem was investigated from the viewpoint of thermodynamics by Wiegand and Snyder[1] and later by Elliott and Lippmann[2], it is still interesting to analyze the problem on a strictly thermodynamic basis, as was done by the authors cited. Elliott and Lippmann, assuming that the internal energy of rubber under slight pressure is a function only of the volume and temperature, arrive at the following equation for the state of rubber, which is not absolutely accurate, as will be shown later:

$$F = T\psi(V, L) \tag{1}$$

GENERAL THERMODYNAMIC RELATIONS

In the deformation of rubber under ordinary conditions, the variable thermodynamic parameters, besides the deformation itself, are the temperature T and the external pressure p, but not the volume V.

Consequently, as a characteristic function the thermodynamic potential should be selected rather than the free energy, as was done by James and Guth[3] and by Guth, James and Mark[4]. As the third independent parameter, Wiegand and Snyder[1], Guth, James, and Mark[4], and Elliott and Lippmann[2] chose the length L of deformation of the specimen. That this is unsatisfactory will be shown later.

In the present work, uniform deformation caused by stretching or compressing a unit mass of rubber was studied. Here f is the applied stress equal to the external force per unit cross-section, for given values of p and T, λ is the relative elongation, equal to $\frac{L}{L_0}$, if $L_0 = L_0(p, T)$ is the length of an undeformed specimen for the given values of p and T. Thus, the value λ indicates the deformation of the rubber.

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by Alan Davis from the *Colloid Journal*, Vol. 70, Part 2, pages 81-87, March-April 1950.

The work of unit compression or elongation of a unit mass of rubber by an external force is equal[5] to $V_0 f d\lambda$, where $V_0 = V_0(p, T)$ is the specific volume of the deformed specimen, and f and λ are general factors well known by analogy with the general thermodynamic functions p and V.

The work of a unit mass of rubber in the general case is:

$$\delta A = pdV - V_0 f \cdot d\lambda$$

where V is the specific volume of the deformed specimen, corresponding to $\lambda = lcV_0$, taking into account that

$$dU = TdS - pdV + V_0 f d\lambda \tag{2}$$

where U and S are the specific internal energy and entropy, respectively, and considering the thermodynamic potential to be a function of p,t, and λ, we find:

$$d\phi = -Sdt + Vdp + V_0 f d\lambda$$

We derive the relation:

$$f = \frac{1}{V_0}\left(\frac{\partial \phi}{\partial \lambda}\right)_{p,T}$$

which gives the equation of the state of rubber in the general form:

$$f = \frac{1}{V_0}\left(\frac{\partial \phi}{\partial \lambda}\right)_{p,T} - T\frac{1}{V_0}\left(\frac{\partial S}{\partial \lambda}\right)_{p,T} + p\frac{1}{V_0}\left(\frac{\partial V}{\partial \lambda}\right)_{p,T} \tag{3}$$

IDEAL RUBBER

As an ideal rubber, analogous to ideal magnetism, we shall consider any rubber for which the internal energy and specific volume do not depend upon the parameter λ,

$$U = U(V,T);\ V = V(p,T) \tag{4}$$

This gives instead of (3):

$$f = -T\frac{1}{V_0}\left(\frac{\partial S}{\partial \lambda}\right)_{p,T} \tag{5}$$

For synthetic rubber, which does not crystallize under pressure, the conditions represented by Equation (4) are fulfilled with great accuracy.

Let us now consider what are the ideal conditions in the case of natural rubber. First of all, since the volume is independent of λ, the following relation holds true:

$$\sigma = \lambda f \tag{6}$$

where σ is the actual stress (the force based on the cross-section of the deformed specimen).

Remembering both conditions of Equation (4) and the thermodynamic relation (2), we next obtain by substitution:

$$dU = \left(\frac{\partial U}{\partial T}\right)_p dT + \left(\frac{\partial U}{\partial p}\right)_T dp;\ dV = \left(\frac{\partial V}{\partial T}\right)_p dT + \left(\frac{\partial V}{\partial p}\right)_T dp$$

the following expression for the differential of entropy:

$$dS = a_1(p,T)dT + a_2(p,T)dp + a_3(p,T,\partial)d\lambda$$

Since dS is the complete differential:

$$\frac{\partial a_3}{\partial T} = \frac{\partial a_1}{\partial \lambda} = 0 \text{ and } \frac{\partial a_3}{\partial p} = \frac{\partial a_2}{\partial \lambda} = 0$$

and from this we derive:

$$a_3 = a_3(\lambda) = - V_0 \frac{f}{T}$$

or

$$f = \frac{T}{V_0(p,T)} \phi(\lambda) \tag{7}$$

where $\phi_{(1)} = 0$. Taking into account Equation 6, it is possible to obtain an analogous expression for the effective pressure.

The function $\phi(\lambda)$ may be derived by determining the molecular-kinetic modulus of the test-specimen of rubber. Wall[6] derived by such a method the equation:

$$\phi(\lambda) = \text{const} \left(\lambda - \frac{1}{\lambda^2}\right)$$

Another equation was derived by the author[7] for not too great deformations:

$$\phi(\lambda) = \text{const} \left(1 - \frac{1}{\lambda}\right)$$

In order to introduce the variables F and L, it should be noted that:

$$f = \frac{L_0(p,T)}{V_0(p,T)} F; \lambda = \frac{1}{L_0(p,T)} L$$

Substitution of these equations in Equation (7) gives:

$$F = \frac{T}{L_0(p,T)} \phi \left(\frac{L}{L_0(p,T)}\right) \tag{8}$$

In Equations 7 and 8 the thermal expansion and compression of the rubber are completely accounted for, and the corrections which were repeatedly introduced because of the misunderstanding of James and Guth[3] Meyer and Ferri[8], and a number of other investigators[9], are unnecessary.

From Equation 8 it follows, for example, that, for slightly stretched rubber, when L is constant, the relation: $L = L_0(p,T)$ may be achieved on heating. Here $\lambda = 1$ and $F = 0$. Therefore, with sufficiently small pressures, the force decreases as the temperature increases, if the length of the specimen remains constant. This fact has been repeatedly observed experimentally. For high pressures, when L is constant, Equation 8 indicates an approximately linear increase of force with temperature.

SEMI-IDEAL RUBBER

For rubber which does not crystallize, the first condition in Equation (4) evidently holds true for any deformation. However, the second condition no longer holds true of high elongations or compression. In this case, instead of condition (4), we have the following conditions:

$$U = U(V,T); V = V(p,T,\lambda) \tag{9}$$

We shall call rubber for which these conditions are valid semi-ideal rubber. Here the free energy $F = U - TS$ must be included as the characteristic function. Regarding it as a function of V, T, and λ, we obtain:

$$dF = -SdT - pdV + V_0 f d\lambda$$

From this follows:

$$f = \frac{1}{V_0}\left(\frac{\partial F}{\partial \lambda}\right)_{V,T} = \frac{1}{V_0}\left(\frac{\partial U}{\partial \lambda}\right)_{V,T} - T\frac{1}{V_0}\left(\frac{\partial S}{\partial \lambda}\right)_{V,T}$$

and

$$-\left(\frac{\partial S}{\partial \lambda}\right)_{V,T} = \left(\frac{\partial V_0 f}{\partial T}\right)_{\lambda,V}$$

Taking into account the first of these conditions in Equation (9), we note:

$$V_0 f = T\left(\frac{\partial V_0 f}{\partial T}\right)_{\lambda,V}$$

This gives the following equation of state:

$$f = \frac{T}{V_0(p,T)}\psi(V,\lambda) \tag{10}$$

Conversion to the variables F and L gives:

$$F = \frac{T}{L_0(p,T)}\psi\left(V, \frac{L}{L_0}\right)$$

instead of Equation (1), found by Elliott and Lippmann, for this case.

REAL RUBBER

Generally, when:

$$U = U(V,T,\lambda);\ V = V(p,T,\lambda)$$

the equation of state is determined from Equation (3). Under the conditions referred to, certain simplifications are possible.

Let us first calculate the term:

$$\left(\frac{\partial V}{\partial \lambda}\right)_{p,T}.$$

Considering the volume a function of p,T,λ, we obtain:

$$dV = \left(\frac{\partial V}{\partial p}\right)_{\lambda,T} dp + \left(\frac{\partial V}{\partial T}\right)_{\lambda,p} dT + \left(\frac{\partial V}{\partial \lambda}\right)_{p,T} \partial\lambda$$

Assuming that $dV = 0$ and $dp = 0$, we obtain the following thermodynamic relation:

$$\left(\frac{\partial V}{\partial \lambda}\right)_{p,T} = -\frac{\left(\frac{\partial V}{\partial T}\right)_{p,\lambda}}{\left(\frac{\partial \lambda}{\partial T}\right)_{p,V}} \tag{11}$$

The term $\left(\frac{\partial \lambda}{\partial T}\right)_{p,T}$ can be determined approximately by the following method.

The stretched specimen of rubber is heated under definite conditions of p, T, and λ to the temperature rise dT. The volume of the specimen is thereby increased (disregarding the anisotropic heat of thermal expansion) by the quantity $dV = V\alpha dT$, where:

$$\alpha = \frac{1}{V_0}\left(\frac{\partial V}{\partial T}\right)_{p,\lambda}$$

The specimen is then compressed[10] to length $d\lambda$ so that its volume decreases to exactly dV. This decrease in volume can be calculated if the Poisson coefficient μ is known.

For purposes of simplification, we shall take a specimen of rubber with a square cross-section. Let δ be one side of the square, and L the length of the stretched specimen.

Determining the Poisson coefficient gives:

$$\mu = -\frac{d\delta}{\delta} \Big/ \frac{dL}{L}$$

Remembering that $V = \delta^2 L$ and $dV = 2\delta L d\delta + \delta^2 dL$, we find that:

$$dV = V(1 - 2\mu)\frac{dL}{L} = V(1 - 2\mu)\frac{d\lambda}{\lambda}$$

From this we derive the following equation:

$$V\alpha dT = -V(1 - 2\mu)\frac{d\lambda}{\lambda}$$

From this it follows:

$$\left(\frac{\partial \lambda}{\partial T}\right)_{p,V} = -\frac{\alpha\lambda}{(1 - 2\mu)}$$

After substituting this value in equation[11] we find:

$$\frac{1}{V_0}\left(\frac{\partial V}{\partial \lambda}\right)_{p,T} = \frac{(1 - 2\mu)}{\lambda} \qquad (12)$$

Using this formula, it is possible to assign a value to the last term in Equation (3). We note that these values apply to crystals, just as Equation (3) is valid for any thermodynamic system.

For many solid materials, the Poisson coefficient is approximately 0.25. Substitution of this value in Equation (12) gives the value $+0.5$, where $\lambda = 1$. Consequently, for crystals the term $p\frac{1}{V_0}\left(\frac{\partial V}{\partial \lambda}\right)_{p,T}$ is approximate.

For rubber, the Poisson coefficient is approximately 0.50. Moreover, as Equation (12) proves, on stretching, the effect diminishes proportionately to λ.

According to data from the experimental laboratory of the MGU Mechanical Institute, the Poisson coefficient of unvulcanized natural rubber containing 2.5 per cent sulfur when stretched up to 40 per cent has an average value of 0.49. For this value, at atmospheric pressure and when $\lambda = 1$, we find:

$$p\frac{1}{V_0}\left(\frac{\partial V}{\partial \lambda}\right)_{p,T} = 0.02 \text{ kg. per sq. cm.}$$

This value, especially for specimens of small cross-section, lies within the precision of measurement of the applied stress. Therefore, the corresponding term in Equation (3) may be disregarded under similar conditions.

The equation of state:

$$f = \frac{1}{V_0}\left(\frac{\partial U}{\partial \lambda}\right)_{p,T} - T\frac{1}{V_0}\left(\frac{\partial S}{\partial \lambda}\right)_{p,T} \tag{13}$$

or

$$F = \left(\frac{\partial U}{\partial \lambda}\right)_{p,T} - T\left(\frac{\partial S}{\partial L}\right)_{p,T} \tag{14}$$

The term $\left(\frac{\partial S}{\partial \lambda}\right)_{p,T}$ for small deformations clearly does not depend on the temperature. This is confirmed, for example, by the calculations of Wall[6] who obtained the following expression for the entropy:

$$S = \frac{N}{2}\left(\lambda^2 - \frac{2}{\lambda} - 3\right) + S_0(p,T)$$

Here N is the number of molecular chains in a unit mass of rubber.

In this case, the term $\left(\frac{\partial S}{\partial L}\right)_{p,T}$ must depend on the temperature. Therefore, Equation (13) is the most suitable in analyzing the equation of state.

The internal energy for the general case is:

$$U = U(0) + \int_0^T C_{V,\lambda} dT$$

where $C_{V,\lambda}$ is the heat capacity at constant volume and constant deformation. It depends in an approximate way on p, T and λ. Disregarding these factors, it is possible to rewrite Equation (13) in the form:

$$V_0 f = A(p,T,\lambda) + B(\lambda)T$$

In this case, if A does not depend on the temperature, there may be a linear dependence on T if λ is constant. This satisfies the requirement that $C_{V,\lambda}$ does not depend on λ, which in turn gives $A = \left(\frac{\partial U}{\partial \lambda}\right)_{p,T} = 0$. This condition brings us back to the case of rubber. If $A \neq 0$, as is true of rubber undergoing crystallization, then A must depend on the temperature.

In this case a determination of $B(\lambda)$ from the slope of the temperature curves is meaningless. However, certain investigators[11] carelessly used this expression for $B(\lambda)$. Furthermore, Wiegand and Snyder have already shown the correct method for determining A and B. For this operation we shall use the thermodynamic equation:

$$\left(\frac{\partial S}{\partial \lambda}\right)_{p,T} = -\left(\frac{\partial V_0 f}{\partial T}\right)_{p,\lambda} \tag{15}$$

After substituting in Equation (13) we find:

$$V_0 f = \left(\frac{\partial U}{\partial \lambda}\right)_{p,T} + T\left(\frac{\partial V_0 f}{\partial T}\right)_{p,\lambda} \tag{16}$$

In these equations, by determining experimentally the dependency of $V_0 f$ on T, for constant p and λ, we may find contradictions between the values of $\left(\frac{\partial U}{\partial \lambda}\right)_{p,T}$ and $\left(\frac{\partial S}{\partial \lambda}\right)_{p,T}$ for the data on rubber.

Since, where $\lambda = 1$ and $f = 0$ for any values of p and T, we find, in accord with Equations (15) and (16) that:

$$\left(\frac{\partial S}{\partial \lambda}\right)_{p,T,\lambda=1} = 0 \text{ and } \left(\frac{\partial U}{\partial \lambda}\right)_{p,T,\lambda=1} = 0$$

Thus in the undeformed state, the entropy, with constant values of p and T, reaches a maximum and the internal energy a minimum.

An equation analogous to Equation (16) was obtained by Wiegand and Snyder for the variables F,L, and $p = 0$, and was applied to the values of ideal rubber from natural rubber.

$$F = \left(\frac{\partial U}{\partial L_{p,T}}\right) + T\left(\frac{\partial F}{\partial T}\right)_{p,L}$$

We shall see what the equation gives for the case of ideal rubber, where:

$$\left(\frac{\partial U}{\partial L}\right)_{p,T} = \left(\frac{\partial U}{\partial \lambda}\right)_{p,T} = 0$$

If L is a constant which differs slightly from L_0, then upon heating it is easy to reach the point $F = 0$ because of thermal expansion. But we have also seen that $\left(\frac{\partial F}{\partial T}\right)_{p,T} \neq 0$. This discrepancy would indicate that the equation of Wiegand and Snyder is inaccurate.

The work of James and Guth[3] and of Guth, James, and Mark[4] is also an example of the loose application of thermodynamics. These authors assumed that the term $\left(\frac{\partial S}{\partial L}\right)_T$ does not depend on the temperature, and this necessarily introduced errors for thermal expansion.

In conclusion, it should be remembered that most studies of rubber are concerned with atmospheric pressure. Therefore, it is possible in the equation of state to disregard the term which depends on the volume. For practical purposes it may be assumed that all rubber behaves ideally if the following conditions are met: $U = U(p,T)$ or its equivalent: $\left(\frac{\partial U}{\partial \lambda}\right)_{p,T} = 0$.

REFERENCES

[1] Wiegand and Snyder, *Trans. Inst. Rubber Ind.* **10**, 234 (1934); RUBBER CHEM. & TECHNOL. **8**, 151 (1935).
[2] Elliott and Lippmann, *J. Applied Physics* **16**, 50 (1945); RUBBER CHEM. & TECHNOL. **18**, 579 (1945).
[3] James and Guth, *J. Chem. Physics* **11**, 455 (1943).
[4] Guth, James, and Mark, in *Advances in Colloid Science*, **2**, 253 (1946): *Chemistry of Large Molecules* **1**, 172 (1948).
[5] This may be proved in a simple way from the following assumptions. Assume that a parallelopiped of unit mass is removed from the sample. The work of the external force then is:

$$FdL = fS_0(p,T)dL$$

where $S_0(p,T)$ is the cross-section of the parallelopiped when not deformed. Noting further that

$$d\lambda = \frac{dL}{L_0(p,T)}$$

where L_0 is the length of the parallelopiped when not deformed, we find:

$$FdL = V_0(p,T)f \cdot d$$

if $V_0(p,T)$ is the specific volume of the undeformed specimen. Since p, T, and L are independent variables, and taking into account the first of these conditions in Equation (9), we note:

$$\lambda = \int_0^L \frac{dL}{L_0(p,T)} = \frac{L}{L_0(p,T)}$$

[6] Wall, *J. Chem. Physics* **10**, 485 (1942); RUBBER CHEM. & TECHNOL. **15**, 806 (1942).
[7] Bartenev, "Investigations in High Molecular Compounds," Academy of Science Press, U.S.S.R. 1949, p. 308.
[8] Meyer and Ferri, *Hel . Chim. Acta* **18**, 570 (1935); RUBBER CHEM. & TECHNOL. **8**, 319 (1935).
[9] Petersen, Anthony, and Guth, *Ind. Eng. Chem.* **34**, 1349 (1942); RUBBER CHEM. & TECHNOL. **16**, 290 (1943); Anthony, Caston, and Guth, *J. Phys. Chem.* **46**, 826 (1942); RUBBER CHEM. & TECHNOL. **16**, 297 (1943).
[10] Or is stretched if, under pressure, the crystalline phase has a higher density than that of the amorphous phase.
[11] Anthony, Caston, and Guth, *J. Phys. Chem.* **46**, 826 (1942); RUBBER CHEM. & TECHNOL. **16**, 297 (1943); James and Guth, *J. Chem. Physics* **11**, 455 (1943).

CHANGE IN THE RELAXATION PROPERTIES OF VULCANIZED RUBBER ON SWELLING *

A. Dogadkin and V. E. Gul

Moscow Institute of Fine Chemical Technology, Im. M. B. Lomonosov, Moscow, U.S.S.R.

In work published by Dogadkin, Bartenev, and Reznikovskiĭ[1], it was shown that the effect of slow relaxation, which is characteristic of highly elastic polymers, is the partial or complete restoration of the balanced configurations of the molecular chains, and that the rate of relaxation is governed primarily by the character of the intermolecular forces in the polymer. On this basis, the kinetics of high-elastic deformations can be expressed by the equation:

$$\frac{d(\sigma - \sigma_\infty)}{dt} = (E_0 - E_\infty)\frac{d\epsilon}{dt} - \frac{\sigma - \sigma_\infty}{\tau} \qquad (1)$$

where σ is the mean stress, σ_∞ is the stress at equilibrium, t is the total time, τ is the time of relaxation, E_0 is the initial modulus of elasticity, and E_∞ is the modulus of elasticity at equilibrium.

This equation is a generalization of Maxwell's well known equation, and it is applicable to the relaxation process if, in conformity with the theory of the authors cited above, it is assumed that the time of relaxation τ depends on the stress in accord with the equation:

$$\tau = \tau_0 \exp\left(U_0 - \frac{V}{2E_1}\sigma_1^2\right)/(kT) \qquad (2)$$

where $\sigma_1 = (\sigma - \sigma_\infty)$ is the unbalanced stress, $E_1 = (E_0 - E_\infty)$; τ_0 is the time of relaxation corresponding to the initial modulus, and U_0 is the energy of activation with respect to the kinetic relaxation factor V.

The applicability of Equations (1) and (2) to rubber and its halide derivatives also was shown. In this case the nature of the structure (in the sense of the number and configuration of the chains) remains unchanged, whereas there is a fundamental change in the intermolecular forces.

Another method of determining the effect of intermolecular forces on the mechanical properties of polymers is to study them in the swollen state, because the process of swelling, although it does not change the molecular structure of a substance, does change fundamentally its intermolecular energy. As a means of studying the mechanical properties of swollen rubber, the apparatus in Figure 1 was designed. In this apparatus, a ring-shaped test-specimen of the sample (1) was stretched by weights on a small carriage (2), running on a rail (3), and enclosed in a double-walled cylinder. The stress was regulated by varying the declination of the cylinder, and was read on scale (4). The elongation was read on scale (5) inside the cylinder. The cylinder, heated to the desired temperature by an ultrathermostat, was filled with a mixture of nitrogen and the

* Translated for Rubber Chemistry and Technology by Alan Davis from the *Reports of the Academy of Sciences*, U.S.S.R., Vol. 70, No. 6, pages 1017–1019, February 21, 1950.

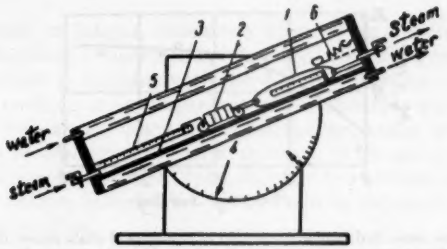


FIG. 1.—Schematic diagram of the apparatus for measuring the mechanical properties of high elastic materials at different temperatures and in different media.

vapor of the solvent. The amount of swelling of the test-specimen was measured by a spring balance (6), inside the cylinder.

Relaxation-pressure curves were obtained by this method for vulcanized natural and polychloroprene rubbers swollen in benzene and in chloroform (see Figure 2). These curves show deviations from the relation assumed by Flory and Rehner[3] between the stress σ for a given distortion of the test-specimen α and its relative swelling v:

$$\sigma = \frac{\rho RT}{M_c v^{1/3}} \left(\alpha - \frac{1}{\alpha^2} \right) \tag{3}$$

The computed equilibrium molecular weight of a chain segment (M_c), measured between two junctures of a spatial network, increases directly with swelling to a definite and constant value (see Figure 3). This effect indicates rupture of local intermolecular bonds under the influence of the solvent.

By means of Equation (2) it was possible to measure the total times of relaxation of the test-specimens.

In the swelling of vulcanized natural rubber in benzene, at a temperature of 24°, the total time of relaxation showed a sharp decrease to a point where the swelling, Q, corresponded to 0.26 mole of benzene in 100 grams of mixture. Then up to $Q = 0.36$ the time of relaxation increased and, finally, with further increased in Q, it decreased. The relation of the time of relaxation to the degree of swelling of natural rubber in chloroform (Figure 4) can be represented in a rough way by the same curve.

To explain the observed variations in the time of relaxation, it is necessary to take into account the heterogeneous structure of the intermolecular bonds of vulcanized rubber.

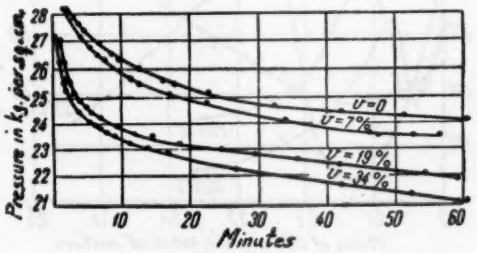


FIG. 2.—Curves of relaxation of pressure of vulcanized natural rubbers in chloroform. V = degree of swelling.

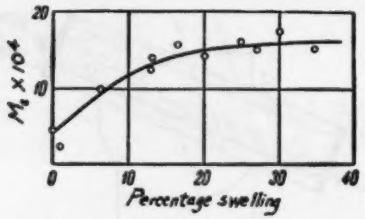


FIG. 3.—Relation of the mean static molecular weight of segments of chain molecules of vulcanized natural rubber located between two junctures of a spatial network, to the degree of swelling in benzene.

On swelling, the molecular activity of vulcanized rubber immediately increases as a result of the increase in the number of possible configurations; but since swelling is accompanied by a simultaneous three-dimensional deformation of the spatial network of the high polymer, the number of possible configurations of the chains decreases. Consequently this process governs the decrease in the activity of the chain molecules at a definite stage of swelling. When swelling is at a maximum, the stress on the chains is increased so much that the local intermolecular bonds which depend on the orientation bonds or hydrogen bonds of the oxygen-bearing and sulfur-bearing groups of vulcanizates begin to be broken. That the molecular activity of the high polymer under these conditions increases is shown by the decrease in the time of relaxation.

This explanation is in harmony with the effect of temperature. A rise in temperature, by decreasing the influence of the intermolecular energy, smooths the curves and displaces the minimum relaxation to lower degrees of swelling.

Swelling of polychloroprene in chloroform is characterized by a steady decrease in the time of relaxation. In this case all the intermolecular bonds seem to be destroyed gradually, since most of them are located close together on chains containing chlorine atoms.

The change in the kinetics of high-elastic deformations observed during swelling is evident also in the process of repeated deformations. The resistance to fatigue of vulcanizates of natural rubber in chloroform, expressed by the logarithm of the number of cycles which the specimen withstands to the point of rupture, decreases at first in proportion to the increase in the degree of swell-

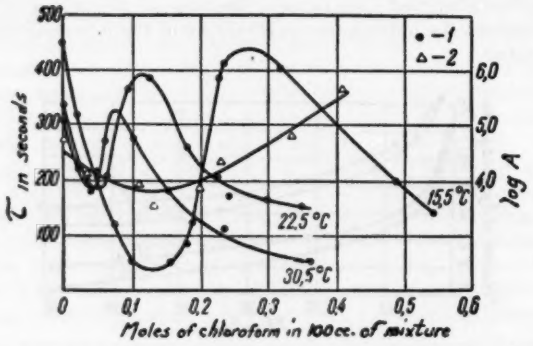


FIG. 4.—Time of relaxation (1) and resistance to swelling (2) of natural rubber in chloroform at different temperatures.

ing. This decrease in fatigue resistance when Q approaches 0.13 mole of chloroform in 100 grams of mixture is in accord with the general tendency of the time of relaxation to increase with increase in the value of Q. The maximum increase in swelling is accompanied by a continuous and noteworthy increase in fatigue resistance. Increase in fatigue resistance begins when a decrease in the time of relaxation is first observed. It should be noted also that the fatigue resistance is influenced, not only by the change in kinetics of the high-elastic deformation, but also by the decrease in the static tensile strength resulting from the swelling.

REFERENCES

[1] Dogadkin, Bartenev and Reznikovskil, *Colloid J.* 11, 5, 314 (1949).
[2] Flory and Rehner, *J. Chem. Phys.* 11, 11, 521 (1943).

ULTRA-SPEED TENSILE OF RUBBER AND SYNTHETIC ELASTOMERS *

D. S. VILLARS

GENERAL LABORATORIES, UNITED STATES RUBBER COMPANY, PASSAIC, NEW JERSEY

INTRODUCTION

A machine has been developed which is capable of recording the stress-strain curve of rubber at rates of elongation up to 9000 times that used in the Scott tensile test. This is over 100 times faster than any rate previously attained in any rubber tests. Availability of such high speed, which shall hereinafter be designated as "ultra speed", enables one now, for the first time, to study the relationship to service behavior of fundamental physical properties of commercial rubber stocks. The present paper presents a brief description of the machine and surveys the speed dependence of tensile strength, elongation at break, modulus, and breaking energy of rubber and synthetic elastomers.

Other investigators have attempted to measure short time stress strain and tensile of rubber. Albertoni[1] described a pendulum impact tester which measured energy expended to stretch individual samples to definite predetermined elongations and to break. Roth and Holt[2] built a clever guillotine type of machine which stretched samples by means of a vertically falling weight. Dart, Anthony, and Wack[3] devised a fast stress-strain machine working on the principle of a mechanical balance.

Objections to the foregoing types of machine are: that (1) the time of break is not short enough; (2) too much calculation is required to obtain the stress-strain curve (excessive calculation precludes large volume of investigation); (3) the rate of elongation in the Roth-Holt machine is not uniform, and (4) a different sample is tested for each point on the stress-strain curve when using the Albertoni machine.

Our present new machine overcomes each of these objections. It gives times of break down to 0.5 msec. with constant rates of elongation almost 100 times that of the Albertoni machine, 200 times the mean rate of the Roth and Holt apparatus, 1000 times that obtained with the highest frequency dynamic hysteresis apparatus (Naunton and Waring[4], about 1000 cycles per sec.), and 9000 times that of the Scott tensile machine. It gives direct photographs of the complete stress-strain curve of a particular sample, without any reduction by integration or differentiation.

DESCRIPTION OF ULTRA-SPEED MACHINE

The machine (*cf.* Figure 1) consists of a rotating wheel, on the circumference of which a pin strikes the middle enlarged part of a double dumbbell test-piece hanging in the form of a loop. This dumbbell was designed expecially for this machine. The two narrow parts are 0.1 inch wide and 17/64 inch long. The

* Reprinted from the *Journal of Applied Physics*, Vol. 21, No. 6, pages 565–573, June 1950. This paper was presented before the Division of Rubber Chemistry, at the 116th Meeting of the American Chemical Society, Atlantic City, N. J., September 21–23, 1949. The present address of the author is U. S. Naval Ordnance Test Station, China Lake, California.

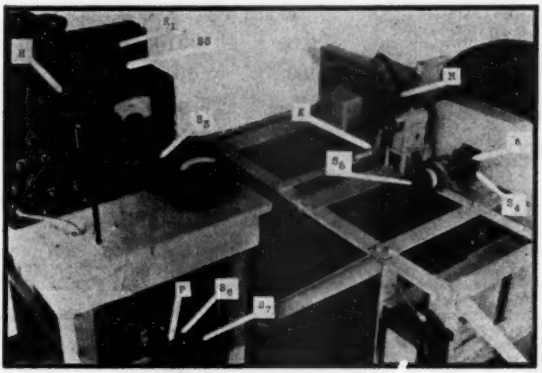


FIG. 1.—Ultra-speed machine.

total length of test-piece is $5\frac{7}{32}$ inches. The stress produced is communicated mechanically to a piezoelectric crystal which generates an electrical potential directly proportional to the stress. This potential is amplified and recorded on an oscillograph screen. The oscillograph trace, which is the stress-strain curve, is photographed on 35-mm. film. Calibration is carried out by suddenly applying a steady force on the crystal by means of an electromagnet. The strength of the latter is in turn determined by weighing the force necessary to break the armature away from the magnet. By means of a variable-speed transmission, and speed-reducing pulleys, all wheel speeds between 60 and 1700 r.p.m. can be obtained. The corresponding elongation rates in rubber samples vary from 9.3 to 270 per cent per msec. The output of the machine is 13 to 16 stress-strain curves per day[5].

STOCKS

Two series of stocks are considered in this paper. In the first, called the "replication series", standard tread stocks containing 50 parts carbon black (per hundred of elastomer), and standard gum stocks, omitting all carbon black, were compounded and cured. The second series is of six different elastomers, without and with 21 volumes of channel black per 100 volumes of matrix (rubber plus soluble components). Table I gives the formulas of the second series.

RESULTS

SHAPE OF STRESS–STRAIN CURVE

A typical ultra-speed stress-strain curve taken at 57 per cent per msec. is reproduced in the upper half of Figure 2. It is approximately linear. Figure 3 plots the average of three stress-strain curves of a rubber gum stock taken at 36 per cent per msec. At the highest ultra-speeds, the stress-strain curves assume a wave form (lower half of Figure 2), sometimes multiple in character. The reason for this multiplicity is not known. It may have something to do with slippage of the samples in the holders. It may be associated with resonance chattering oscillations in the crystal holder or crystal itself. That it is not due to each wave representing individual nonsimultaneous breaks of the two sample sides was shown by the fact that samples with one side cut beforehand also showed double loops.

TABLE I

	ADJ	ADK	ADL	ADM
Pale crepe	100	100		
GR-S			102	102
Blended black		47		46
Stearic acid	2	5	1.5	1.5
Zinc oxide (XX)	5	8	5	5
Antioxidant[a]	1	1		
Captax[b]	1	1	1.5	1.5
Sulfur	2.5	2.5	1.5	1.5
Cure	35 min. @ 30 lb.	30 min. @ 40 lb.	30 min. @ 50 lb.	45 min. @ 50 lb.

	ADN	ADO	ADP	ADQ
Hycar-OR	100	100		
GR-I			101.5	101.5
Blended black		44		46
Stearic acid	1	1	3	3
Zinc oxide	5	5	5	10
Age-rite powder	1	1		
Altax[c]	1	1		
Tuex[d]			1	1
Sulfur	1	1	0.5	1.5
Cure	30 min. @ 50 lb.	30 min. @ 50 lb.	30 min. @ 50 lb.	45 min. @ 55 lb.

	ADR	ADS	ADT	ADU
Perbunan	100	100		
Neoprene-GN			100	100
Blended black		44		35
Stearic acid	1.5		0.5	0.5
Lauric acid		1.5		
Zinc oxide	5	5	1	1
Extra light calcined magnesia			4	4
552 accelerator[e]			0.5	1.5
Neozone-A[f]			2	2
Altax[c]	1	1.25		
Sulfur	1.2	1.25		
Cure	15 min. @ 50 lb.	45 min. @ 50 lb.	15 min. @ 50 lb.	30 min. @ 45 lb.

[a] Reaction product of acetone and a diarylamine.
[b] 2-mercaptobenzothiazole.
[c] Bis-2-thiobenzothiazole.
[d] Tetramethylthiuram disulfide.
[e] Piperidine salt of *N,N*-pentamethylenedithiocarbamic acid.
[f] Phenyl-β-naphthylamine.

VELOCITY OF SOUND

At the greatest ultra-speeds, the possibility has been taken into consideration of perturbing effects which might be introduced by the wave character of stress response whenever the rate of elongation approaches too closely the velocity of sound in the sample. For zero hysteresis, the stress recorded at the held end of a uniform sample elongated at a constant rate should increase with time by finite perpendicular steps[6]. Although we know that we are dangerously near the velocity of sound at highest speeds, no elastomer curves have yet been observed which have the step shape predicted by wave theory. This fact indicates that none of our conclusions are subject to modification because of wave

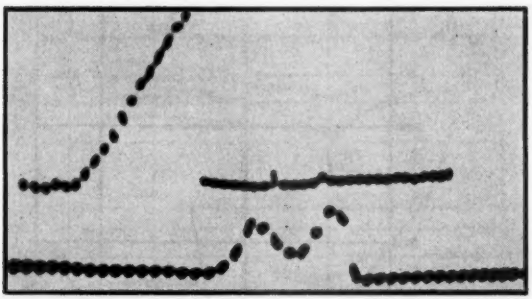


FIG. 2.—Ultra-speed stress-strain curves. Upper curve: rubber tread; elongation rate, 57 per cent per msec.; timing frequency, 2000 c.p.s.; tensile strength, 3530 lb. per sq. in.; elongation at break, 325 per cent; time of break, 5.7 msec. Lower curve: special rubber tread; elongation rate, 238 per cent per msec.; timing frequency, 5000 c.p.s.; tensile, 6600 lb. per sq. in.; elongation at break, 143 per cent; time of break, 0.6 msec.

phenomena. However, it is still possible that large specific acoustic absorption effects at the frequencies concerned might reduce the steepness of the steps. This could result in the steps being overlooked.

PREWORKING

The possibility of an effect of preworking was checked by running a series of rubber tread stocks, half of the samples of which were preworked by (hand) stretching ten times out to the hardening point and back. The order of testing these and unworked controls was random. Results (Table II) indicate no great effect on either tensile or elongation.

COMPARISON OF HIGH AND LOW SPEED STRESS–STRAIN CURVES

Figure 3 compares the average of three ultra-speed curves (elongation rate 36 per cent per msec.) of rubber gum stock with a slow-speed stress (single pull —no preworking) strain curve of a sample from the same slab of rubber, as recorded by an autographic stress strain machine designed by H. M. Smallwood, H. T. Battin, and W. Moorman. This machine uses ring-shaped test-pieces, 1.373 inches outside diameter and 1.173 inches inside diameter. Such test-pieces never give the full value of the tensile strength, probably "because of uneven distribution of stress over the cross-section caused by the fact that the inside of the ring is stretched more than the outside during elongation and because of the effect of the clamp pulleys on the portions of the ring passing over them"[7]. However, the autographic curve (Figure 3) is seen to head for the

TABLE II

EFFECT OF PREWORKING RUBBER TREAD
Mean time of break, 8 msec.

	Tensile strength		Elongation	
	Unworked	Preworked	Unworked	Preworked
	2910	3180	442	540
	2790	2610	442	388
		2010		334
Mean	2850	2600	442	421

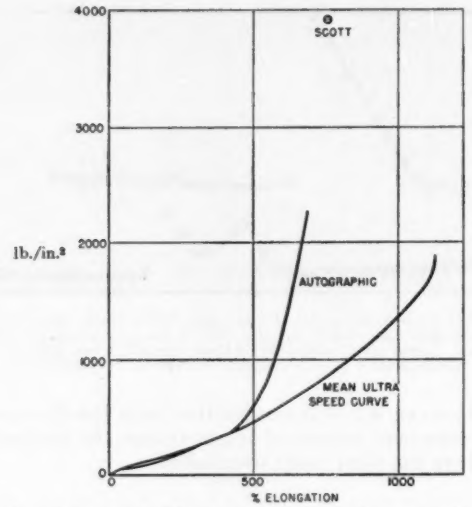


FIG. 3.—Comparison of ultra-speed with autographic stress-strain curve—rubber gum. Times of break—ultra-speed, 28 msec.; Scott: 30 sec.; autographic: 88 sec.

Scott tensile value, also determined on pieces from the same slab. It breaks away from the ultra-speed curve at about 400 per cent elongation.

REPRODUCIBILITY OF MEASUREMENT

To obtain an accurate estimate of the variability of measurement, triplicate mixes of Hevea and GR-S gum and tread stocks were mixed in random order and cured. Each test slab was $6\frac{1}{2} \times 6\frac{1}{2} \times 0.1$ inches, and supplied five ultra-speed stress-strain, four Scott, and one autographic stress-strain test-pieces. In this test, five speeds were investigated, and each mix-speed combination was run in random order until each combination was represented. Such a block was then repeated in a new random order until five blocks were completed.

In carrying out such a program plan, stress-strain curves are occasionally missed. This is sometimes caused by faulty synchronization, sometimes by failure of the sweep trigger mechanism, not to speak of human failures to open the camera shutter or turn the film on to the next frame. Such missing values were filled in by the method of Yates[8].

The standard deviations of testing error were determined separately for each individual rate of elongation (see Table III). It may be seen from the I-shaped marks on Figure 4(a) that the standard deviation of tensile strength

TABLE III

TESTING ERROR OF ULTRA-SPEED TENSILE STRENGTH—QUARTZ CRYSTAL
Tread stocks—AKE-I.

Elongation rate (per cent per msec.)	Standard deviation (lb. per sq. in.), mean of five
11	80
24	120
55	170
120	305
260	370

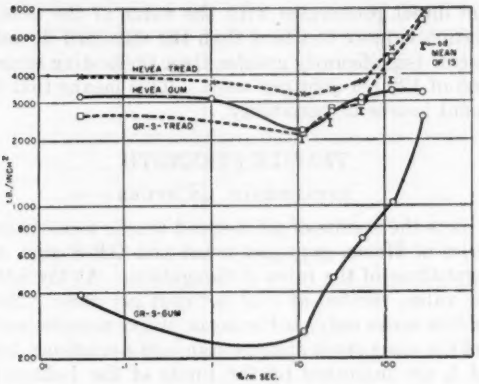


FIG. 4(a).—Tensile strength—Replication series AEG-J.

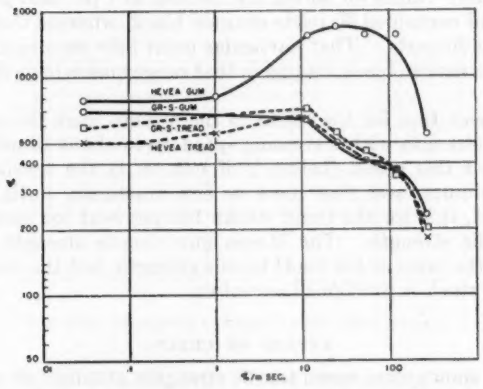


FIG. 4(b).—Elongation at break—Replication series AEG-J.

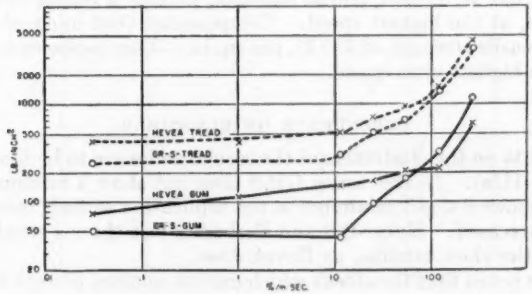


FIG. 4(c).—Modulus—Replication series AEG-J.

tends to vary in direct proportion with the value of the tensile strength (coefficient of variation is more constant than the standard deviation).

No mixing error (significantly greater than the testing error) was found except at the speed of 120 per cent per msec. This means that the testing error is the predominant source of variability.

TENSILE STRENGTH

DEPENDENCE ON SPEED

Figure 4(a) plots the results of ultra-speed tensile measurements on the first (replication) series of Hevea gum and tread and GR-S gum and tread. The abscissas are logarithms of the rates of elongation. At the left of the graph is the Scott tensile value, plotted at 0.03 per cent per msec. Each of the ultra-speed values (in this series only) is the mean of five samples each of three independent mixes of the same stock and the standard deviations, listed in Table III as for means of 5, are indicated by the limits of the I-shaped figures on the graphs (after converting to means of 15). From these limits one may judge visually the significance of the trends exhibited.

Roth and Holt[2] values for Hevea are inserted at 1 per cent per msec. Their tread compound contained 40 parts channel black, whereas that in the present work contained 50 parts. That particular point falls reasonably on our curve, as if variation in carbon black loading in that range makes little difference at that low a speed.

It may be seen that for the stocks in the present work there is a significant drop in tensile strength with increasing speed up to about 10 per cent per msec. Somewhere near this speed (before it if not at it) the tensile strength goes through a minimum, and rises more or less drastically until, at the highest speeds observed, it is for the tread stocks 100 per cent (or more) greater than the Scott tensile strength. The Hevea gum tensile strength at the highest speed is about the same as the Scott tensile strength, but the tensile strength of the GR-S gum stock is multiplied sevenfold.

EFFECT OF CURING

Figure 5(a) shows ultra-speed tensile strengths obtained on raw Hevea gum and tread stocks. The samples for these runs were interspersed in random order among those of the replication series. It may be seen that raw smoked sheet, which has zero Scott tensile strength, attains a tensile strength of 900 lb. per sq. in. at the highest speed. Compounded (but uncured) tread stock has a Scott tensile strength of 530 lb. per sq. in. This increases to 4200 lb. per sq. in. at the highest ultra-speed.

DEPENDENCE ON ELASTOMER

Tensile data on the elastomers of the second series are to be found plotted in Figures 6(a)–11(a). In this series GR-S does not show a minimum in tensile strength (it shows a slight minimum in the replication series), but a steady rise as speed is increased. Hycar-OR and Perbunan also show a steady rise. The other synthetics show minima, as Hevea does.

It is to be noted that the stocks which exhibit minima (except for GR-S) are ones which are known to crystallize at ordinary slow rates of stretching. The other stocks do not crystallize. The minimum in the first GR-S series may be related to an orientation of lower order than crystallization.

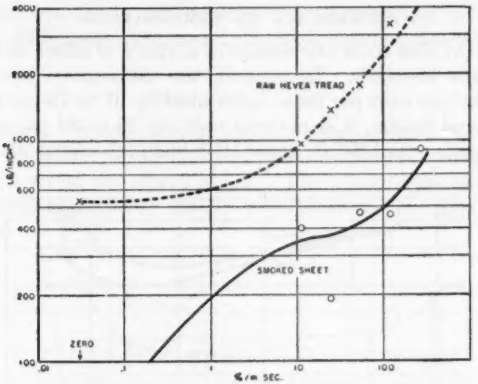


FIG. 5(a).—Tensile strength—unvulcanized Hevea.

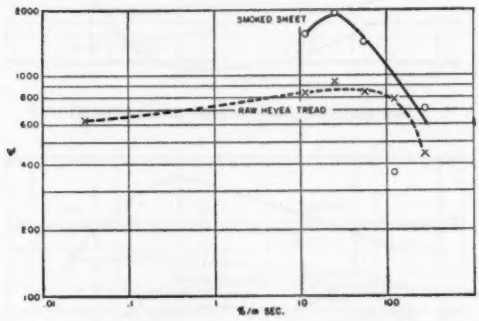


FIG. 5(b).—Elongation at break—unvulcanized Hevea.

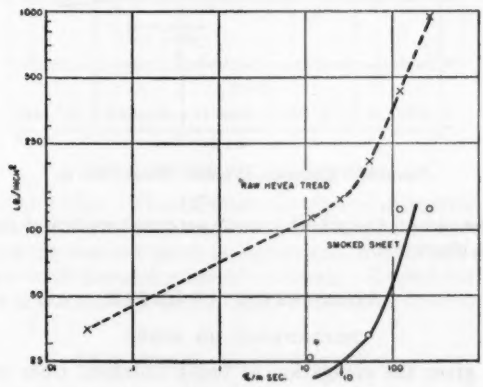


FIG. 5(c).—Modulus—unvulcanized Hevea.

DEPENDENCE ON TEMPERATURE

Figures 6–11(a) also show the results of a study of effect of temperature on ultra-speed tensile strength. In general, the ultra-speed tensile strength of gum stocks at 240 per cent per msec. is reduced by 67 to 75 per cent by heating to 150° C; of tread stocks, it is reduced only by 20 to 50 per cent (exception: possibly Perbunan). At 150° C, gum GR-S has such a poor ultra-speed tensile

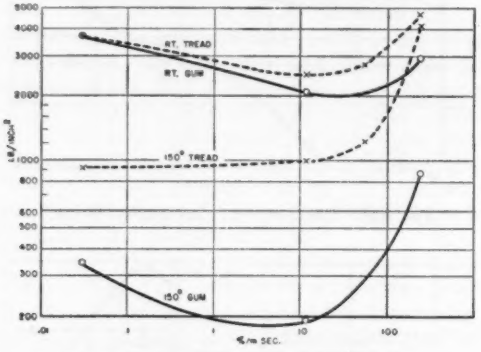


FIG. 6(a).—Tensile strength—Hevea ADJ, K.

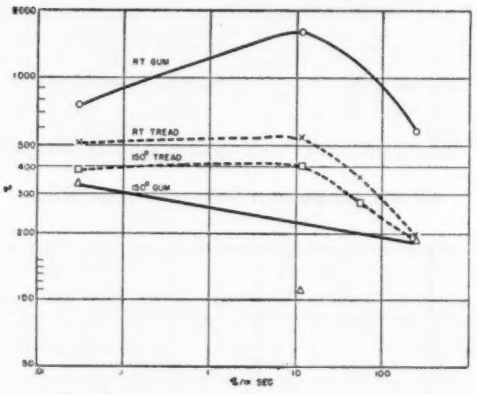


FIG. 6(b).—Elongation at break—Hevea ADJ, K.

strength that the pin on the wheel knocks an exact replica of the pin out from the sample by a clean cut.

ELONGATION AT BREAK

DEPENDENCE ON SPEED

Figure 4(b) gives the elongation at break obtained from measurement of the replication series. It shows at 1 per cent per msec. elongation values of Roth and Holt. The Hevea stocks, especially the gum, show a maximum in elongation at break twice that at Scott speed, between 10 and 30 per cent per

msec. The GR-S stocks do not exhibit this phenomenon to so marked an extent, if at all. At highest ultra-speed, all stocks become drastically shortened.

EFFECT OF CURING

See Figure 5(b). Elongation at break of the uncured smoked sheet and tread compound shows curves similar to those of the cured stocks, except for an upward displacement of the stread stock. The ultra-speed values of the uncured smoked sheet agree fairly closely with those at the same speeds for the cured gum stocks.

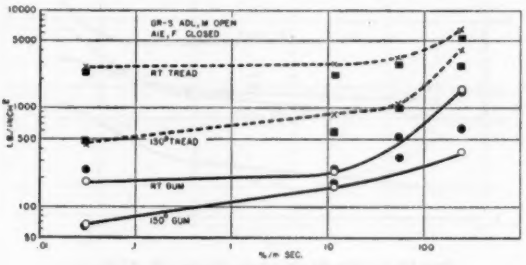


FIG. 7(a).—Tensile strength—GRS. ADL, M; AIE, F.

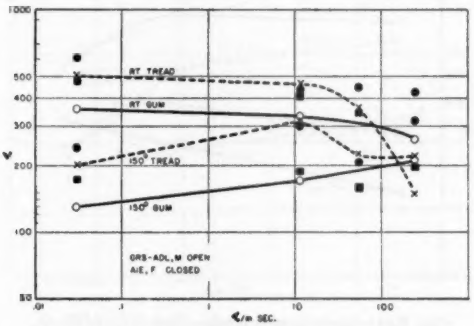


FIG. 7(b).—Elongation at break—GRS. ADL, M; AIE. E

DEPENDENCE ON ELASTOMER

See Figures 6(b)–11(b). The different elastomers, in general, are classifiable into two groups: one in which the elongation at break passes through a maximum at an intermediate ultra-speed (such as Hevea and Butyl) and one for which it steadily decreases with increasing speed of break. Except for Neoprene-GN, this classification is the same as that of elastomers which do or do not crystallize on stretching.

DEPENDENCE ON TEMPERATURE

Ultra-speed elongation at break at 150° seems, in general, to be greater for tread stocks than for gum stocks at all speeds except the highest. Heating to 150° reduced elongation of all stocks except the Butyl tread.

MODULUS

The ultra-speed modulus was computed from the tensile strength and elongation at break with the approximation that the ultra-speed stress-strain curve is linear. For Scott speed, the modulus was arbitrarily taken as the slope of the line between the origin of the (single-pull) autographic stress-strain curve and the point of inflection. This value thus does not include the subsequent increase in modulus which many elastomer stocks undergo at higher elongations (usually ascribed to orientation). It lies between the Wall-Young's modulus and the shearing modulus as computed from Young's modulus by

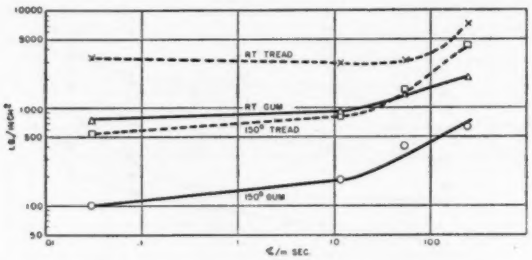


FIG. 8(a).—Tensile strength—Hycar OR. ADN, O.

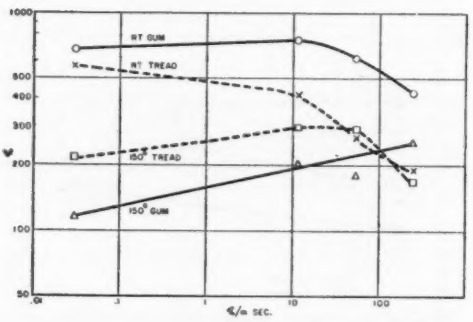


FIG. 8(b).—Elongation at break—Hycar OR. ADN, O.

dividing the latter by three. Within this range, the comparability of the low speed values with the ultra-speed values is somewhat uncertain.

DEPENDENCE ON SPEED

Figure 4(c) gives modulus measurements obtained from the replication series. It contains at 1 per cent per msec. modulus values of Roth and Holt. Modulus is almost independent of elongation rate up to 10 per cent per msec., above which speed it rises rapidly.

EFFECT OF CURING

The moduli of uncured smoked sheet and of uncured tread compound show curves similar to those of the cured stocks, except for a downward displacement in value (see Figure 5(c)).

DEPENDENCE ON ELASTOMER

Plots of moduli of the elastomer series, in general, show that modulus is more or less constant until ultra-speeds are reached, when it starts to increase with an accelerated pace.

DEPENDENCE ON TEMPERATURE

The modulus of gum stocks is little affected by increasing temperature to 150°; that for tread stock is shifted to the side of higher rates of elongation. Exceptions to this last generalization are Hevea and Neoprene, where the curves for tread stocks rise to the same modulus at highest speed.

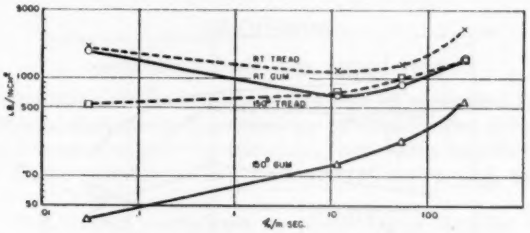


FIG. 9(a).—Tensile strength—Butyl. ADP, Q.

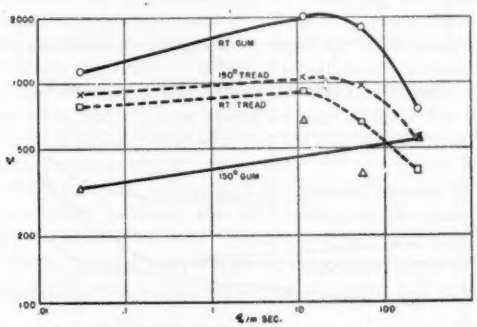


FIG. (9b).—Elongation at break—Butyl. ADP, Q.

ENERGY OF BREAK

Ultra-speed energy of break was computed from the tensile strength and elongation at break with the approximation that the ultra-speed stress-strain curve is linear. For Scott speed, energy of break was obtained by integrating (by planimeter) the complete single-pull autographic stress-strain curve after extending it to the Scott tensile strength and elongation at break. The slow-speed energy thus includes the contribution of all orientation effects. Energy of break values appears to be subject to an excessively large error. They fluctuate so greatly that no trends with speed appeared significant.

INDEPENDENT DETERMINATION OF ENERGY OF BREAK

Energy of break was checked independently by measuring the instantaneous drop in wheel speed occurring when the sample is broken. This was measured

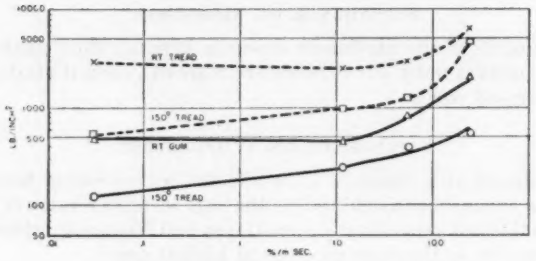


FIG. 10(a).—Tensile strength—Perbunan. ADR, S.

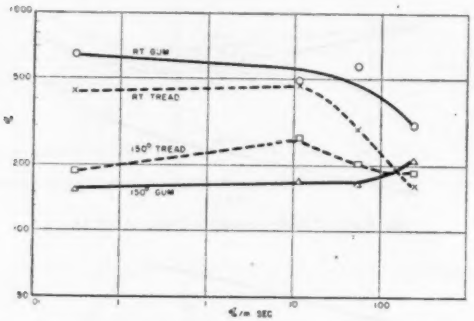


FIG. 10(b).—Elongation at break—Perbunan. ADR, S.

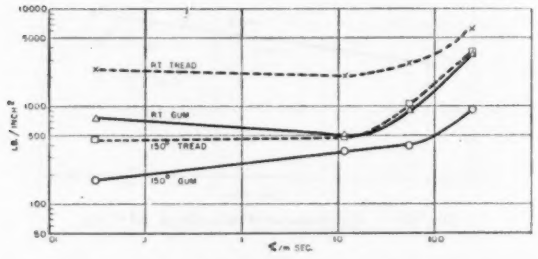


FIG. 11(a).—Tensile strength—Neoprene-GN. ADT, U.

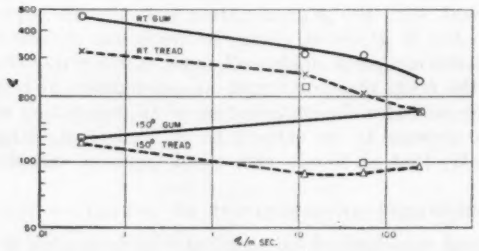


FIG. 11(b).—Elongation at break—Neoprene-GN. ADT, U.

by connecting the oscillograph to give a changing pattern, the frequency of which was the difference between the wheel frequency and an adjustable reference frequency. The difference between this difference frequency before and immediately after breaking a sample was combined with the moment of inertia of the wheel to compute the energy of break.

Two values obtained are 18.5 and 15.6 ft.-lb. for the rubber tread. These values, determined at 25 cycles per sec. wheel speed, are to be compared with the total energy of break, 10.12 ft.-lb., given by a stress-strain curve at 23 cycles, of a similar sample. The latter figures include 1.69 ft.-lb. kinetic energy of the end thrown off. The high tensiles indicated by our measurements of the stress-strain curves are thus independently confirmed.

DISCUSSION

CRYSTALLIZATION AND RELAXATION

In explaining the observed effects of the rate of elongation on the stress-strain properties of elastomers, it is necessary to consider two phenomena which can be induced in an elastomer by stretching, but which require finite time for completion. These phenomena are, first, crystallization and, second, relaxation.

The fact that rubber crystallizes on stretching is familiar to all rubber chemists. Many, if not most, attribute the upbend in the ordinary stress-strain curve to onset of crystallization. According to Acken, Singer, and Davey[9], a minimum time of the order of 1.2 seconds is required after stretching before enough crystallization develops to show up in an x-ray picture. As our ultra-speed curves are produced in times of lower order of magnitude than this, it is plausible to attribute differences between those obtained at the lesser ultra-speeds and those obtained at slow speed to lack of time for crystallization to develop. This lack of time would account for the approximate linearity of the ultra-speed stress-strain curves.

This theory may be used to account for the differences in tensile strength and elongation at break between the slow autographic stress-strain and the mean ultra-speed curve of Figure 3. Since the latter was produced in an average time of 28 msec., presumably much too short for crystallization, we may conclude that crystallization increases tensile strength but shortens the elongation at break.

A corollary of the hypothesis of a finite time requirement for completion of crystallization is of interest in problems of abrasion resistance. Inasmuch as abrasion processes generally occur in cycles shorter than 20 msec., it appears questionable whether the crystallization characteristics of a tread stock can have any direct effect on its abrasion resistance.

Relaxation, the second phenomenon invoked to explain the ultra-speed results, is the loss of stress with time in a sample held at a constant deformation. It is thought to be due to a slow intermolecular slippage within the rubber, accompanied sometimes by a reversible, sometimes irreversible, breaking of bonds. Kuhn[10] and others have suggested that many properties of rubber may be explained by postulating more than one type of slippage bonds, the different types being distinguished by different relaxation rate constants.

Now if the time of test is made shorter than the relaxation time of the rapidly relaxing components, they contribute more and more toward the total modulus. This is how we account for the increase in modulus as rate of elonga-

tion increases to 200 per cent per msec. and greater. The increase in tensile strength with increasing speed implies that the slipping bonds also add to strength when not given time to slip.

The minima in tensile strength and maxima in elongation observed with crystallizing stocks now may be interpreted as the point of balance between decreasing importance of crystallization and increasing importance of slipping bonds that fail to slip as speed is increased. If the 90 per cent drop in tensile of gum Hevea which is observed at Scott speed on heating from room temperature to 150° is a measure of the contribution of crystallinity, the formation of only about one-third of the total crystallinity is prevented by stretching at the lower ultra-speeds.

On the slipping bond hypothesis, the rate of elongation at which the sharp rise occurs, 200 per cent per msec., qualitatively gives the order of magnitude of the relaxation time as 0.5 msec. It is believed that many service processes may occur within times of this order of magnitude. For example, Markwick and Starks[11] report high frequency oscillations of 1400 cycles per sec. in tread rubber retracting from a dry road. As far as we know, no one has reported confirmation of this observation, and it may possibly be a spurious mechanical effect. However, if an important part of the strength of a stock originates from rapidly relaxing elements, it is clear that a completely successful correlation between laboratory and service can never be expected until the time of test is reduced to that characteristic of the service condition.

HEAT OF ACTIVATION OF SLIPPAGE

If the above hypothesis is true that the rise in modulus and tensile may be attributed to bonds, which ordinarily completely relax within the time of stretching, not having time to relax completely at the higher ultra-speeds, then it would be reasonable to expect a particular curve to shift bodily to the side of higher elongation rate on going to higher temperature. Since if one used as abscissas the parameter, speed/relaxation rate (or speed × relaxation time), an increase of temperature increases the rate of relaxation. Hence to find the same modulus, one should look for it at a greater speed. A complete shift of the curve without change in shape is too much to expect, inasmuch as it could occur only in the unlikely event of only one type of relaxation. With more than one type, the modulus contribution of each would be shifted by a different amount corresponding to its different change in rate of relaxation. This would bring about a change in shape of the composite curve which is the sum of the individual components.

We have noted the above shift in the case of carbon black stocks. A heat of activation may, therefore, be roughly computed from the ratio of rates at 150° and at room temperature. A list of such values is given in Table IV.

TABLE IV

HEAT OF ACTIVATION OF RELAXATION RATE IN TREAD STOCKS

Elastomer	ΔH(kg.-cal.)
Hevea	3.08
GR-S	3.67
Hycar-OR	3.75
Butyl	3.77
Perbunan	2.78
GR-M	1.57

It may be seen that the heat of activation is of the order of magnitude of 3 kg.-cal. This may be compared with 10.3 kg.-cal. heat of adsorption of benzene on graphite[12] (the nearest similar process to adsorption of rubber on carbon black on which there are published data), 10 kg.-cal. heat of activation of shear in raw rubber[13], 15 kg.-cal. for shear in raw GR-S[14], 15 kg.-cal. for transient relaxation in cured rubber, and 15 kg.-cal. for steady relaxation in cured rubber[15]. The considerably lower value of 3 kg.-cal. is in accord with a "slide-fastener" mechanism of slippage of rubber molecules along a carbon black surface proposed by the present author. In this mechanism the attached segments of rubber are supposed to slip with moderate resistance along the surface of the black from one end to the other without pulling away free from it. When the rubber-black bond reaches the end of the "zipper", it is fairly permanently resistant to complete separation.

The failure to find a shift in the gum-stock curves means, on the above hypothesis, that the heat of activation of slippage for the other types of slippage is very low; *i.e.*, the relaxation rates involved have too low a temperature coefficient to be measurable within the accuracy of the experiment.

SUMMARY

A high speed stress-strain machine has been developed which is capable of recording the stress-strain curve of elastomers at elongation rates up to 270 per cent/msec. Data are reported on two series of gum and tread stocks of Hevea and of the synthetic elastomers, GR-S, Hycar-OR, Butyl, Perbunan, and Neoprene-GN. The second (elastomer) series was also run at 150° C. In general, stress-strain curves fall into two classes. Stocks of elastomers which are known to crystallize on stretching tend to show tensile strengths which decrease with increasing speed up to about 10 per cent/msec., pass through a minimum, and rise more or less drastically to values 100 per cent (or more) greater than the Scott tensile strength. Elastomers which do not crystallize on stretching tend to show a steady rise in tensile strength with increasing speed. Elongation at break curves show a maximum with crystallizing stocks and no maximum with noncrystallizing stocks. The shape of the modulus *vs.* speed curves is accounted for on the hypothesis of different types of slipping bonds with different characteristic relaxation times. The shift of curves for tread stocks with temperature allows the estimation of a heat of activation of slippage. This comes out to be of the order of 3 kg.-cal.

ACKNOWLEDGMENT

Appreciation is herewith expressed to the various members of the staff who have been consulted in the development of the machine; in particular to E. M. Grabbe, M. Mooney, and S. A. Black. R. B. Frost designed and supervised the original construction of the machine and T. J. Rhodes designed several of the later modifications. The experimental work of operating the machine was carried out by O. K. Laible.

REFERENCES

[1] Albertoni, *Ind. Eng. Chem. Anal. Ed.* **9**, 30 (1937); Rubber Chem. & Technol. **10**, 317 (1937).
[2] Roth and Holt, *J. Research Natl. Bur. Standards* **23**, 603 (1939); Rubber Chem. & Technol. **13**, 348 (1940).
[3] Dart, Anthony, and Wack, *Phys. Rev.* **69**, 52A (1946).
[4] Naunton and Waring, *Proc. Rubber Technol. Conf., London*, **1938**, p. 805.
[5] It is planned to submit a detailed technical description of the machine to the *Review of Scientific Instruments*.

[6] Fourier analysis of the equation:

$$(\partial^2 y/\partial \tau) = (\partial^2 y/\partial \xi^2)$$

for the boundary conditions:

$$\begin{aligned} y &= 0 \text{ at } \tau = 0 \\ (\partial y/\partial \tau) &= 0 \text{ at } \tau = 0 \\ y &= 0 \text{ at } \xi = 0 \\ y &= \alpha\tau \text{ at } \xi = 1, \tau > 0 \end{aligned}$$

gives:

$$y = \alpha\xi\tau + \frac{2\alpha}{\pi^2} \sum_{m=1}^{\infty} \frac{(-1)^m}{m^2} \sin m\pi\xi \sin m\pi\tau$$

In these equations, the dimensionless quantities are defined as:

$$y = u/L; \xi = x/L; \tau = t/(L/v); \alpha = a/v$$

where u is the displacement of a point in the sample of total length L, originally at a distance x from the fixed end, t is time, a is the uniform velocity of displacement of the other end of the sample, and v is the velocity of sound in the rubber (taken as constant). The local elongation: $\partial y/\partial \xi$ at $\xi = 0$ (and hence stress) may be shown to represent a series of perpendicular steps, each of height 2 dimensionless units and of length 2 units of τ.

[7] Carpenter, in "The Chemistry and Technology of Rubber", New York, 1937, p. 791.
[8] Yates, *Empire J. Expil. Agr.* 1, 129 (1933).
[9] Acken, Singer, and Davey, *Ind. Eng. Chem.* 24, 54 (1932); RUBBER CHEM. & TECHNOL. 5, 30 (1932).
[10] Kuhn, *Z. physik. Chem.* 42B, 1 (1939).
[11] Great Britain Department of Science, "Report of Road Research Board for the Year ending March 31, 1939", p. 150; Markwick and Starks, *J. Inst. Civil Eng.* (London) 16, 309 (1941).
[12] Harkins and Boyd, *J. Am. Chem. Soc.* 64, 1195 (1942), Table 3.
[13] Smallwood, *J. Applied Physics* 8, 505 (1937).
[14] Mooney, M., private communication.
[15] Mooney, Wolstenholme, and Villars, *J. Applied Physics* 15, 324 (1944).

THE MECHANISM OF THE ACTION OF AROMATIC THIOLS ON RUBBER SOLUTIONS *

E. P. KHERASKOVA AND A. P. GAMAYUNOVA

MOSCOW INSTITUTE OF FINE CHEMICAL TECHNOLOGY, MOSCOW, U.S.S.R.

It has been found possible to accelerate the plasticization of natural Hevea rubber by means of the addition of aromatic thiols during the plasticizing process. This method is known as chemical plasticization.

The mechanism of such chemical plasticization has not hitherto been explained, although the following facts may be considered to be already well established. (1) Thiols accelerate the high-temperature plasticization of rubber, which itself is a result of oxidation of the rubber at elevated temperatures[1]. These facts have been confirmed by an investigation made by Dogadkin and associates[2], which show that films of rubber oxidize much more rapidly in the presence of oxygen. (2) Thiols accelerate the decrease in viscosity of rubber solutions brought about by heating the latter.

A technological study of the plasticizing action of thiols on rubber during milling, carried out in our laboratory under the direction of Professor F. F. Koshelev, proved inadequate for explaining the process involved in chemical plasticization, and it was evident that a more accurate method of investigation would have to be carried out before such a complex problem could be solved. In the present work the method of measuring the viscosity of rubber solutions heated in the presence of aromatic thiols was selected for study.

The rubber solutions were heated in the apparatus shown in Figure 1. A 5 per cent solution of rubber in xylene was put in the flask, and a current of air from the inlet was slowly passed through. The flask was immersed in an oil thermostat, and at regular intervals during the heating, samples were removed from the solution for viscosity measurements. The viscosity was expressed by the time of flow in seconds of the solution through a capillary tube. To eliminate the effects of sunlight on the process, the entire experiment was carried out under a steady electric light.

Preliminary experiments showed that the rate of change of viscosity of the rubber solution in the presence of a thiol does not, in general, depend on the type of natural rubber. Most of the experiments were carried out with smoked-sheet rubber; in the experiments where analytical determinations were to be made, pale crepe, which gave colorless solutions in xylene, was used.

The following thiols were tested in the experiments: xylenethiol (a mixture of isomers), mercaptobenzothiazole, α-naphthylenethiol, and 2,4-toluenedithiol.

Since there is no reason to doubt that the SH group is the reactive group in all the thiols, it may be assumed that the mechanism of their action in rubber solutions does not differ from one thiol to another. However, it should not be concluded that the chemical structure of a thiol does not influence its activity. In the experiments of the present work, we did not attempt to study the in-

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by Alan Davis from *Colloid Journal* 12, No. 2, pp. 146–153 (1940).

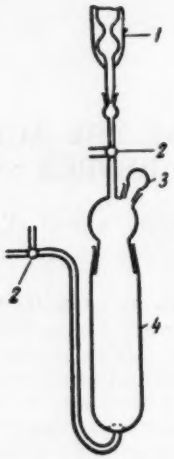


FIG. 1.—Apparatus for heating rubber solutions:
1. condenser 3. opening for making tests
2. 3-way cock 4. receptacle

fluence of the structure of different thiols in a rubber solution; rather, we studied the mechanism of the action of the SH group, which is common to all thiols.

With the object of maintaining the same conditions with all the thiols, the concentration of SH groups for each thiol in 1 gram of rubber (1 mg. equivalent) was computed.

EXPERIMENTAL PART

The effect of thiols on the viscosity of rubber solutions.—The experiments indicated that all thiols diminish the viscosity of rubber solutions to approximately the same extent (see Figure 2). The intensity of the effect of the thiol on the rubber solutions increased with increase in the concentration of the thiol and with rise in temperature (see Figures 3 and 4).

The curves shown in these figures indicate that the rate of change in the viscosity of rubber solutions under the influence of thiols diminishes with time. The greatest rate of fall in viscosity was observed at the beginning of heating; subsequently the rate gradually decreased, and, after reaching a definite value, remained practically constant.

Chemical changes in thiols in the process of heating in rubber solutions.—Inasmuch as the effectiveness of a thiol depends on its concentration in the solution, it appeared that there might be a correlation between the kinetics of the diminishing fall of viscosity and the gradual disappearance of thiol in the solution. If so, the concentration of thiol in the descending section of the curve must approach zero.

The introduction of a supplementary amount of thiol into the solution in which this rapid fall in the viscosity has ended would be expected to lead to a renewed sharp decrease in viscosity. This was confirmed by experiments in which the thiol was added several times to the same solution (see Figure 5).

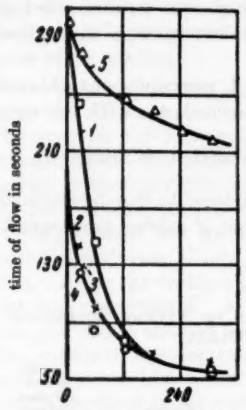


FIG. 2.—Change in viscosity of rubber solutions in the presence of different thiols, at 80° C; thiol concentration of 0.1 mg.-equiv.

1. mercaptobenzothiazole
2. xylenethiol
3. α-naphthylenethiol
4. 2,4-toluenedithiol
5. nothing added

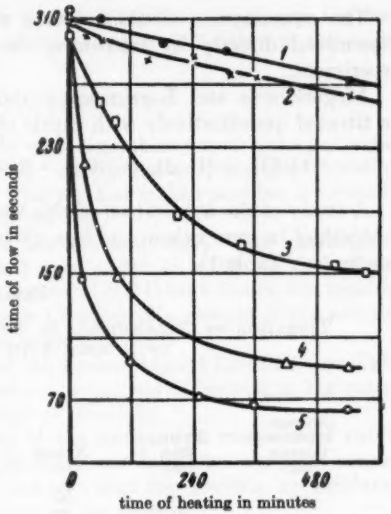


FIG. 3.—Change in the viscosity of rubber solutions in the presence of different concentrations of xylenethiol at 40°.

1. no thiol
2. 0.01
3. 0.03
4. 0.6
5. 1.2 mg.-equiv. of xylenethiol

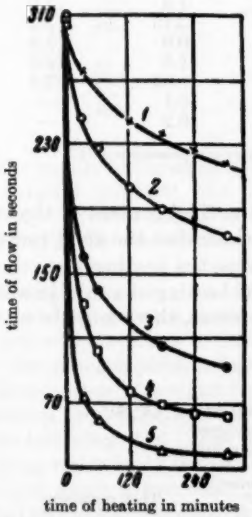


FIG. 4.—Change in viscosity of rubber solutions in the presence of xylenethiol of different concentrations.

1. without thiol
2. 0.01
3. 0.05
4. 0.1
5. 0.03 mg.-equiv. xylenethiol

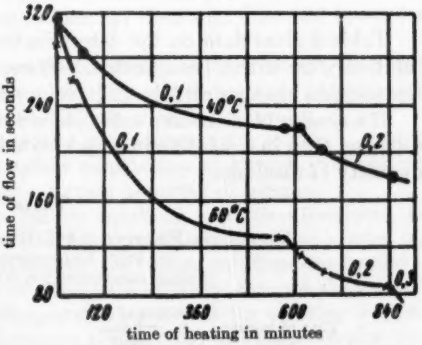


FIG. 5.—Change in the viscosity of rubber solutions in the presence of repeated additions of xylenethiol. The initial thiol concentration, 0.15 mg.-equiv. was successively increased to 0.2 and 0.3 mg.-equiv.

The consumption of thiol during the heating of a rubber solution was determined directly by measuring the thiol concentration throughout the experiment.

Mogoricheva and Korsunskaya[3] showed that mercaptobenzothiazole can be titrated quantitatively with cupric oleate in accordance with the equation:

$$4RSH + (C_{17}H_{33}O_2)_2Cu \rightarrow RSSR + 2CuSH + 4C_{17}H_{33}O_2H$$

A study of the application of this titration method to the determination of xylenethiol in pure xylene and in a xylene solution of rubber gave satisfactory results (see Table 1).

TABLE 1

TITRATION OF XYLENETHIOL IN XYLENE AND IN XYLENE SOLUTIONS OF RUBBER WITH COPPER OLEATE

Mercaptobenzothiazole (mg.)	Xylenethiol (cc.)	Xylene (cc.)	0.5% rubber solution (cc.)	Cupric oleate solution (cc.)	Cupric oleate solution per mg. equivalent of thiol (cc.)
—	—	50	—	0.1	—
—	—	50	—	0.1	—
—	—	50	—	0.15	—
28.5	—	50	—	2.1	12.3
36.6	—	50	—	2.7	12.1
29.5	—	50	—	2.15	12.2
—	20.7	50	—	1.87	12.4
—	20.7	50	—	1.87	12.4
—	20.7	50	—	1.8	12.0
—	41.4	50	—	3.75	12.5
—	10.4	50	—	0.9	12.0
—	20.7	—	50	1.8	12.0
—	20.7	—	50	1.85	12.3
—	—	—	50	0.1	—
—	—	—	50	0.2	—

The equivalent weight of xylenethiol was 139; that of mercaptobenzothiazole was 167.

Table 2 gives data on the determination of the thiol content of the rubber solution after it had been heated. These data show that the thiol content of the solution changes rapidly and profoundly during the heating.

If a similar phenomenon takes place during the heating of a thiol in a rubber solution, then in a solution in which no thiol is present, there must be an equal quantity of disulfide.

TABLE 2

EFFECT OF HEATING 0.5% RUBBER SOLUTION AT 60° C ON THE XYLENETHIOL CONTENT
(Initial concentration 0.6 mg. equivalent)

Time of heating (min.)	Volume of rubber solution (cc.)	Cupric oleate solution* (cc.)	Thiol remaining (%)
0	50	1.85	100
15	50	0.4	14.7
60	50	0.15	0

* The control solution consumed 0.15 cc.

The reduction of the disulfide with hydrogen iodide according to the reaction below was investigated for proof of the presence of disulfide in the rubber solutions after heating.

$$RSSR + 2HI \rightleftarrows 2RSH + I_2$$

The reaction was reversed, and only with a great excess of hydrogen iodide could the disulfide be completely restored. The iodine was titrated with sodium thiosulfate in the conventional way. This method makes possible the calculation of the disulfide content within ±3 per cent.

The experiment was carried out in the following way. The quantities of mercaptobenzothiaole shown in Table 3 were added to a 0.5 per cent rubber solution. After the solution had been heated at 60° C for 6 hours, the disulfide content was determined. A preliminary titration of a sample of the solution with copper oleate showed the absence of thiol.

The results of the determination of the benzothiazolyl disulfide (see Table 3) lead to the conclusion that the thiol in the process of heating in the rubber solution is oxidized to an equal quantity of disulfide.

The decrease in the kinetic curves of the decrease in viscosity of rubber solutions under the influence of thiol indicate, not only that the thiol concentration decreases during this process, but also that the disulfide accumulating in the system does not have any influence on the process.

TABLE 3

Mercaptobenzothiazole (mg.)	Rubber solution (cc.)	0.3 *N* sulfite (cc.)	Disulfide computed from the theoretical content (%)
—	50	0.3	—
30.1	50	6.0	95
13.5	50	3.0	98.5
40.9	50	8.3	97.7

The results of the experiment in Figure 6 show that, in contrast to the thiol, its oxidation product[4], like pure benzothiazolyl disulfide, does not lower the viscosity of rubber solutions.

Effect of the concentration of oxygen on the energy of the reaction of the thiol.—Experiments made in an atmosphere without oxygen are very important in explaining the mechanism of the action of thiols in rubber solutions.

As an inert gaseous medium, chemically pure nitrogen was chosen. Despite the precautions taken to assure complete elimination of oxygen, we assumed that the nitrogen obtained contained a certain quantity of oxygen.

Elimination of oxygen from the rubber solutions and the subsequent experiments on the thermal behavior of the solutions in nitrogen were carried out in the following way. The flask containing the rubber solution was heated in a boiling-water bath; then a current of nitrogen was passed through the solution until the solution was cool. The heating and cooling of the solution were repeated twice. Continuing to pass nitrogen through the solution, samples were taken for the determination of the initial viscosity; thiol was added, and the flask was immediately put in a thermostat.

Figure 7 shows the change in viscosity of the solution under these conditions. The data for this experiment indicate that the decrease in the con-

centration of oxygen in the rubber solution diminishes significantly the reactivity of the thiol with the rubber.

To ascertain the changes in the concentration of thiol in the experiment conducted in an atmosphere of oxygen, the rubber solution, prepared just as in the preceding experiment, was heated for a given length of time, the flask was opened, and the whole solution was titrated with copper oleate. The viscosity of the solution had already been determined. For purposes of comparison, data for the change in viscosity of the rubber solution when heated in air under identical conditions are included (see Table 4). When the concentration of oxygen in the surrounding medium is decreased, the rate of fall in viscosity of the rubber solution decreases markedly, although a significant quantity of the thiol is present throughout the experiment.

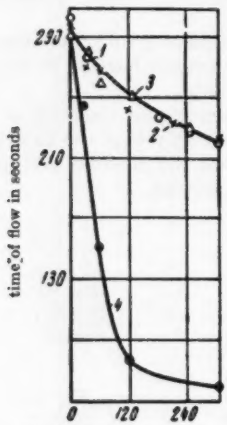


FIG. 6.—Change in viscosity of rubber solutions by the addition of different substances.
1. no thiol
2. oxidized mercaptobenzothiazole
3. benzothiazolyl disulfide
4. mercaptobenzothiazole

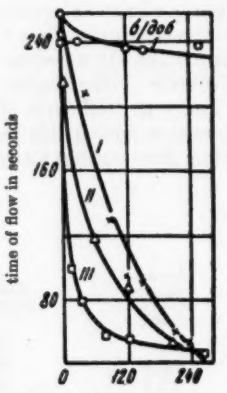


FIG. 7.—Change in viscosity of rubber solutions in the presence of xylenethiol.
I and II in nitrogen
III in air

The experiments in nitrogen lead to the conclusion that the thiol assists in the oxidation of the rubber.

The dependence of oxidation of rubber in solution on oxidation of the thiol.—Investigators who have studied the mechanism of the action of thiols on rubber have assumed that thiols are catalysts of the oxidation of rubber. From this point of view, oxidation of a thiol must lessen its reactivity with rubber, since, as a result of oxidation of the thiol, its concentration in the reacting medium is greatly diminished.

However, a series of observations indicates that the mechanism of the action of thiols does not agree with the classic concept of catalysis, and that the process of oxidation of rubber is closely related to the oxidation process of the thiol itself. Thus, in Figure 2 the curve of change in viscosity of the rubber solution in the presence of mercaptobenzothiazole should be noted. The latter lowers the viscosity of the rubber solution more slowly than do other thiols. A study of the rate of consumption of mercaptobenzothiazole during heating proved

that its oxidation is noticably slower than, for example, that of xylenethiol (see Table 5). These considerations indicate that the acceleration of the oxidation of rubber is influenced, not by the mere presence of a thiol in the reaction medium, but rather by the process of oxidation.

TABLE 4

CHANGE IN CONCENTRATION OF XYLENETHIOL AND VISCOSITIES * OF A 0.5 PER CENT RUBBER SOLUTION ON HEATING AT 60° C
(Initial xylenethiol concentration 0.6 mg. equivalent)

Time of heating (min.)	Quantity of rubber solution (cc.)	Quantity of cupric oleate (cc.)	Viscosity in seconds	
			In nitrogen	In air
0	50	1.85	422	410
30	50	1.65	411	108
45	50	1.6	322	94
180	50	1.65	345	—
240	50	1.55	250	71

* The initial viscosity of a 5 per cent solution of pale crepe rubber was higher than that of a comparable solution of smoked sheet rubber.

Investigations of the process of simultaneous oxidation of rubber and a thiol make it seem likely that two mutually related parallel processes are involved, and that rapid oxidation of the thiol accelerates the otherwise relatively slow oxidation of the rubber, so that, in the presence of the oxidizing thiol, the rate of oxidation of the rubber sharply increased. It appears that such an explanation of the apparent catalytic action of the thiol on the oxidation of rubber is the most probable one.

TABLE 5

OXIDATION OF MERCAPTOBENZOTHIAZOLE IN A 0.5 PER CENT RUBBER SOLUTION AT 60° C
(Initial thiol concentration, 0.6 mg. equivalent)

Time of heating (min.)	Quantity of solution (cc.)	Cupric oleate solution* (cc.)	Remaining thiol (%)
0	50	1.83	100
15	50	0.95	47.6
60	50	0.5	20.8
120	50	0.3	8.9
		0.15	0

* The control solution consumed 0.15 cc.

Thiols are energetic reducing agents because of their chemical nature. As is also well known, thiols are used in the paint industry as antioxidants[5] for protecting paints from drying out. It is assumed that they reduce according to the following equation the hydroperoxides formed from oils:

$$R-OOH + 2R' - SH \rightarrow H_2O + R' - S - S - R' + R - OH$$

It would appear that thiols must behave with respect to rubber according to the same pattern insofar as the formation of hydroperoxides as the first stage of oxidation is concerned. For this reason it seems to the present authors that the concept of a close relation between the oxidation of a thiol and the oxidation of rubber is in harmony with the catalytic influence of the thiol, with its clearly demonstrated reducing properties, on the oxidation of rubber.

All observations up to this point concerning the thermoplasticization of rubber were concerned only with the oxidation of rubber in solution. To prove that, in the technical process of plasticizing rubber in the presence of thiols, the same phenomenon are involved, certain confirmatory experiments on the plasticization of films of rubber at 120° C in an air thermostat were carried out, and it was found that the same regularity occurs as in the oxidation of rubber solutions.

CONCLUSIONS

1. The effect of aromatic thiols on the kinetics of the change in viscosity of natural-rubber solutions on heating was studied.

2. Aromatic thiols accelerate the oxidation of rubber.

3. In the process of heating rubber solutions, thiols are oxidized to the corresponding disulfides. The rate of oxidation of the rubber depends on the rate of oxidation of the thiol.

4. The mechanism of the action of thiols is explained by the presence of an accompanying reaction, whereby oxidation of the thiol induces oxidation of the rubber.

REFERENCES

[1] Busse and Cunningham, *Proc. Rubber Technol. Conf. London*, 1938, p. 288; RUBBER CHEM. & TECHNOL. 12, 163 (1939).
[2] Dogadkin, Karmin, Dobromyslov, and Saposhkova, *Colloid J.* (U.S.S.R.) 10, 268 (1948); RUBBER CHEM. & TECHNOL. 23, 563 (1950).
[3] Mogoricheva and Korsunskaya, *J. Rubber Ind.* (U.S.S.R.) 10, 341 (1933).
[4] The oxidation product of mercaptobenzothiazole was prepared by boiling a xylene solution of mercaptobenzothiazole.
[5] Denison and Condit, *Ind. Eng. Chem.* 11, 1102 (1945).

CRYSTAL VIOLET, AN ELECTRONIC MODEL SUBSTANCE FOR RUBBER AND RELATED OLEFINS *

G. J. VAN VEERSEN

RUBBER FOUNDATION, DELFT, HOLLAND

INTRODUCTION

The use of model substances in chemical practice is well known. If for some reason a definite answer cannot be obtained from experiments concerning a certain compound, the scientific worker is compelled to make use of model substances. The choice of a model substance is based on similarity in molecular structure to that of the compound under investigation. For example, to elucidate the vulcanization reaction of rubber with sulfur, substances such as 2-methyl-2-butene, methylcyclohexene, and dihydromyrcene have been studied. The advantage of using these model substances is that the products resulting from the reaction between the olefins and sulfur can be separated, which is impossible in the case of rubber. For the study of the overall reaction, the use of such model substances based on similarity of molecular structure is advantageous. However, by using these model substances, insight is not always obtained into the reaction mechanism, which is desirable in physical organic chemistry.

Although knowledge of the molecular structure of a compound is of importance, in recent years the electronic structure of a molecule has come more to be the center of interest. In modern organic chemistry the electronic structure of a molecule, in which donor and acceptor properties[1] play an important role, is often a basis of the explanation of its properties (reactivity, color, etc.). As an example, we mention the color of iodine shown in different solvents. The brown color of iodine in alcohol or ether is explained by the assumption that the solvent molecules furnish π-electrons for the formation of a weak bond with the more or less polarized iodine molecule, which acts in these cases as an electron-seeking agent[2]. Evidence for the existence of complex compounds in a solution of iodine in benzene has been given by Benesi and Hildebrand[3] by means of absorption measurements. Thus the fact that the color of iodine changes from red-violet to brown-violet in the series benzene, toluene, xylene, mesitylene finds a satisfactory, albeit qualitative, explanation.

It has been known for a long time that in organic chemistry a great many reactions proceed through reaction intermediates. Apart from those reaction intermediates, such as "transition state" (Polanyi) or "activated complex" (Eyring), which are assumed to exist, although their physical reality has not been proved by independent experiments, a considerable number of complex coördinate compounds of different stabilities are found in the literature, which are frequently assumed to be intermediates in organic reactions. Since we are mainly interested in polar reactions of olefins in this paper, this type of reaction will be discussed briefly.

* Reprinted from *Recueil des Travaux Chimiques de Pays-Bas*, Vol. 69, No. 2, pages 175–191, February 1950. This paper represents Communication No. 112 of the Rubber Foundation, Delft, Holland.

It is generally accepted that donor olefins react with polar agents (hydrogen halides, halogens. Friedel and Crafts catalysts, atomic oxygen) in the polarized state. In the first stage of the reaction a coördinate complex is formed. The formation of such a coördinate complex proceeds in general rapidly, with the evolution of a certain amount of heat. Formulated generally:

$$\text{Olefin} + A \leftrightarrows (\text{Olefin}:A) + \text{q. cal.}$$

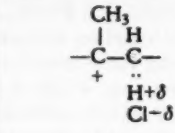
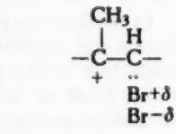
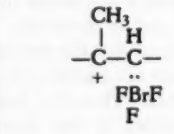
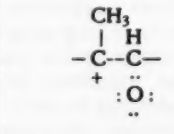
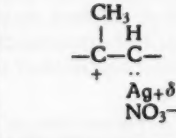
Then by a slower rearrangement of the complex, the final products are formed.

From thermochemical[4] and theoretical[5] considerations, it is evident that, in the formation of a coördinate complex and in the case of alkylethylenes, the less substituted carbon atom carrying π-electrons reacts with the acceptor, *i.e.*, with the more positive atom of the reagent or with the atom bearing a sextet.

The double bond in rubber is spectroscopically, and consequently in energy, identical with monoölefins[6]. The same type of reaction intermediates as shown in Table 1 may, therefore, be assumed in reactions with rubber.

Tentative formulas of coördinative complexes are shown in Table I.

Table I[8]

Chemical agent	coordinative complex
Hydrogen halides[9]	
Halogens[10]	
Friedel and Crafts catalysts[11]	
Oxygen[12]	
$AgNO_3$[13]	

Generally the formation of coördinate complexes in the case of monoölefins is invisible to the human eye. Actual changes in color take place in the ultraviolet region.

The question arising in the mind of the author was the following. If we wish to know how a chemical agent attacks rubber or a related olefin, why should we not make use of another π-electron donor, of which the shift in absorption of light, caused by complex formation, lies in the region of 4000 to 8000 Ångstrom units and effectively enables us to observe visually the formation of such a complex.

The background of this idea was that the electronic theory allows us to consider the π-electrons of donor olefins[7] and aromatic compounds, and, further, the unshared electrons of oxygen and tervalent nitrogen from the same point of view. Since the substance which we want for our purpose must be colored and be provided with suitable donor properties, in principle colored aromatic compounds like naphthacene or oxygen- or nitrogen-containing dyes might be used. Incidentally the well known dye, crystal violet, proved to be very useful in this respect.

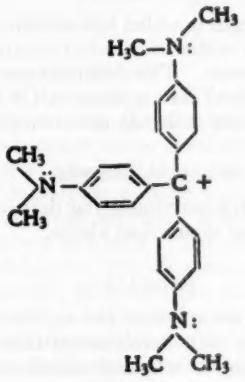


Fig. 1

FIG. 1.

In this paper it will be shown, by means of a series of test-tube experiments, that crystal violet is a suitable electronic model substance to give us insight into reactions of donor olefins in general and rubber in particular.

REACTIONS WITH CRYSTAL VIOLET

Crystal violet (hereinafter referred to as CV), whose formula is shown in Figure 1, is a triphenylmethyl dye. Its deep blue violet color in solution is explained by assuming that the π-electrons at the nitrogen atoms in the dimethylamino groups increase the number of electronic configurations between which resonance of the dye ion is possible, and thus lower the mean energy difference between the ground state and the excited states of the molecule. On interaction of CV with a chemical reagent, a change in electronic structure takes place, with a resultant shift in color which depends on the type of chemical reagent. A classification of chemicals causing specific changes in the color of CV will now be summarized.

POLAR AGENTS

If one equivalent of a mineral acid is added to a solution of CV, the color changes from blue to green (malachite green); if more acid is added, to yellow (fuchsonimid), due to the fact that the contribution of the π-electrons on the nitrogen atoms to resonance is diminished, and causes a reversion of the spectrum to the colorless triphenyl compound. Those acids which cause a change in color from blue to yellow attack CV at the three tertiary nitrogen atoms[14], which is quite understandable, since H-acids can function as acceptors and amines as donors. Since Lewis acids such as $AlCl_3$ or BF_3 are pronounced acceptor molecules, the same explanation holds[15]. Characteristic of this type of color shift is its reversibility, already shown by Rosenstein and Adams[14]. This phenomenon is of special interest to us and, therefore, is described in more detail in this section. Here it may be said that the results of the experiments induce us to assume that a reversible shift in color from blue to yellow caused by some chemical indicates that this reagent belongs to the polar class of reagents.

BASIC AGENTS

If a base of sufficient strength is added to a solution of CV, *e.g.*, sodium hydroxide to a solution of CV in water or di-*n*-butylamine to a solution of CV in toluene, the blue color disappears. This phenomenon is explained by the fact that the electron-deficient central carbon atom in CV is saturated, thus partly breaking conjugation in the dye molecule and removing the absorption from the visible region.

REDUCING AGENTS

On reduction of CV, the triphenylmethane derivative is formed, which is colorless for the same reason as mentioned above.

RADICALS

If solutions of CV in organic solvents are exposed to ordinary light in an atmosphere containing oxygen, slow decoloration takes place. In the absence of light, the rate of decoloration is retarded considerably. Antioxidants like α-naphthol also have a strongly retarding effect on the decoloration of solutions of CV in, *e.g.*, toluene. The addition of peroxides and the use of ultraviolet light or heat, on the other hand, increases the rate of decoloration. Since Wieland and Maier[16] have shown that benzophenone is one of the decomposition products of triphenyl hydroperoxide; and, moreover, CV, if exposed to light and oxygen over a long period, gives Michler's ketone[17] the assumption may be that slow decoloration of CV under conditions favorable for the presence of radicals means that CV is attacked irreversibly by this type of chemical reagent.

REVERSIBLE REACTIONS OF CV WITH ACCEPTOR MOLECULES

We shall now describe a few reactions of CV with hydrogen halides, Friedel and Crafts catalysts, halogens, oxygen, sulfur, and silver nitrate, all of which are reversible.

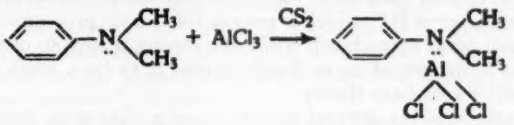
HYDROGEN HALIDES AND FRIEDEL AND CRAFTS CATALYSTS

Hydrogen chloride gas led into a solution of CV in monochlorobenzene turns the blue color to yellow. If such a yellow colored solution is heated at about 80° C, a change in color from yellow to blue is observed, which means dissociation of the CV—HCl complex. Cooling this solution causes a change in

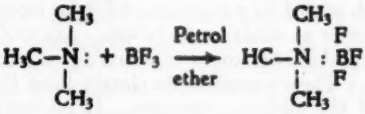
color from blue to yellow, but on heating again the blue color reappears, thus showing the reversibility of the color shift. Addition of generalized acids, *e.g.*, boron trifluoride as etherate, to a blue solution of CV in toluene, causes a change from blue to yellow, with formation of a precipitate. On heating the yellow color remains, which means that dissociation of the CV—BF_3 complex takes place at higher temperatures than in the case of, *e.g.*, hydrogen chloride.

Evidence for the structure of CV complexes with generalized acids has been given by the preparation and investigation of analogous compounds[18]:

1)



2)



and by spectroscopic measurements[19].

Since the temperature of dissociation of CV—HCl in a solvent depends also on the pressure of hydrogen chloride gas, and the dissociation of the complexes of CV with generalized acids could not be observed in solvents, we have tried to determine the temperature at which all these coördinate compounds dissociate in the solid state. For this purpose we used a method which is reminiscent of the way in which Paneth detected radicals. A few drops of a solution of CV in alcohol were introduced into a test-tube. The solvent was evaporated in such a manner that the inner wall of the test-tube was covered with a thin blue layer of CV. Thoroughly dried HF, HCl, BF_3 gas, and liquid $SnCl_4$, were brought into the tube at about $-40°$ C. After the color of CV had turned to yellow, nitrogen gas was slowly led through the tube to remove excess of hydrogen halide and BF_3. Excess of $SnCl_4$ was removed by evacuating and warming the tube. The temperature of the yellow complex was then slowly increased, and the changes in color observed. On heating, the yellow color gradually changed to green, which turned slowly to blue as the temperature increased. The changes in color can be observed with ease, and are fairly reproducible under moisture-free conditions. In the case of $AlCl_3$, $FeCl_3$, $TiCl_4$ and H_2SO_4, difficulties were encountered in observing the temperature of dissociation, partly due to carbonization of the organic part of the complex.

The results are shown in Figure 2.

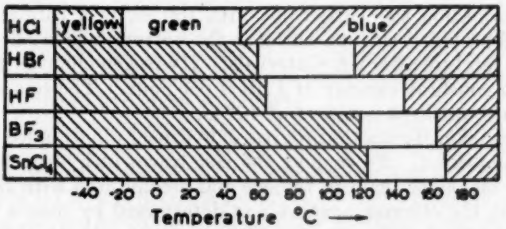


FIG. 2.—Temperature of dissociation of some crystal violet complexes.

Figure 2 shows that the temperature of dissociation of the CV complexes investigated increases in the series HCl, HBr, HF, BF_3, $SNCl_4$, which indicates an increase in acceptor function in the same sequence. This only holds a priori for CV as the referent base[14]. HF is found to be a stronger acceptor than HCl or HBr, which is in line with the facts, that (1) HF is a Friedel and Crafts catalyst in olefin chemistry, and (2) HF cyclizes rubber, whereas HCl and HBr add readily to the double bond. The fact that hydrogen fluoride is a stronger acceptor than hydrogen bromide and hydrogen chloride, though it is known to be a weaker acid than these two hydrogen halides, is explained by the strongly ionic character of HF, which is responsible for its pronounced acceptor function (hydrogen-bond formation), while the strong tendency of the fluorine atom to hold the hydrogen atom so firmly causes it to be a weak acid in the sense of Brönstedt's acid-base theory.

Organic acids in general do not cause a change in color of CV. Only trichloroacetic acid, added to a solution of CV in monochloro-benzene, turns the blue of CV to green at room temperature. On cooling to about −60° C, the yellow appears, and this changes to green again at room temperature, and to blue on heating. These experiments clearly show the effect of temperature on the formation of the addition complex. It proves that the formation of the complex is exothermic.

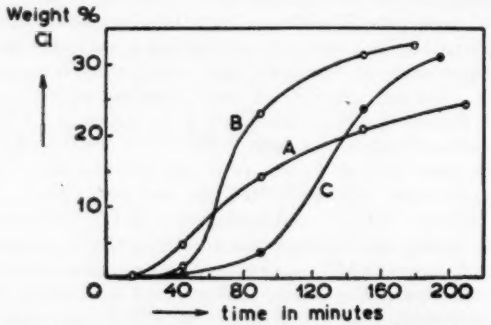


FIG. 3.—Hydrochlorination of rubber in solution. A: rubber in toluene. B: rubber in toluene-ethyl acetate (2:1 vol.). C: rubber in toluene-dioxane (2:1 vol.).

Another similarity between the reactivity of the double bond in rubber and the nitrogen atoms in CV may be pointed out. The following experiments with rubber and CV have been carried out[20]:

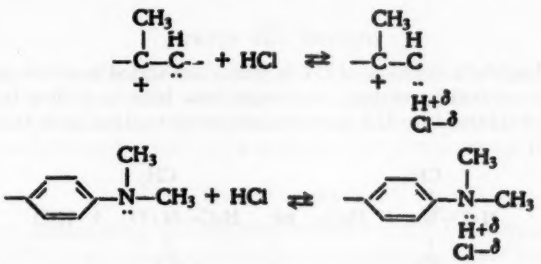
Five per cent solutions of milled smoked sheet in toluene, toluene-ethyl acetate (2:1 vol.) and toluene-dioxane (2:1 vol), respectively, were prepared. The hydrochlorination was carred out with 100 cc. of a rubber solution in a jacketed vessel provided with an outlet in the bottom, which allowed sampling of the reaction mixture after time intervals. Hydrogen chloride gas was passed through with a constant velocity of 4 liters per hour. The temperature of the reaction mixture was kept constant at 10° C.

The samples taken during the progress of hydrochlorination were precipitated with alcohol and dried. To remove the last traces of hydrogen chloride, the products were dissolved again in toluene and precipitated with alcohol. After drying in vacuo the chlorine content was determined by means of the Carius method or by heating with aniline[21]. The results are shown in Figure 3.

If we direct our attention to the beginning of the reaction, we observe that, with toluene as a solvent, the addition of hydrogen chloride to rubber begins shortly after commencing the passage of hydrogen chloride through the solution. In toluene-ethyl acetate and toluene-dioxane mixture, however, the reaction is first delayed for a certain time and then proceeds at a high rate. This time lag is due to the fact that the solubility of hydrogen chloride in ethyl acetate and dioxane is much greater than in toluene.

If hydrogen chloride is passed through a rubber solution, both solvent and rubber molecules compete for hydrogen chloride. The greater the solubility of HCl in a solvent, the more the formation of the rubber-HCl complex and, consequently, the hydrochlorination of the rubber is delayed. Figure 3 shows that the retarding effect on the formation of the rubber-HCl complex is in the order: toluene > ethyl acetate > dioxane.

The following experiment was carried out with CV under the same conditions as with rubber. If hydrogen chloride gas is passed through a solution of CV in toluene, an almost immediate change in color from blue to yellow is observed. With ethyl acetate as a solvent, hydrogen chloride gas must be passed in for a certain time before the shift in color takes place. In dioxane, a still greater time lag is observed. These experiments show that the formation of the hydrogen chloride complexes is influenced in the same way by the solvents used:



Though the donor properties of toluene and ethyl acetate are different towards hydrogen chloride, as shown by the different solubilities of the acid in these solvents, it may be concluded that the donor properties of the double bond in rubber and CV are of the same order.

In principle, these experiments could have been carried out with some generalized acid. However, as it is our purpose to show similarities between rubber and CV and the hydrochlorination of rubber can be followed easily, whereas the reaction between rubber and, *e.g.*, BF_3 has a more complex character, we have chosen the former reaction. This enables us to add the following conclusion. Dipole measurements of hydrogen chloride in carbon tetrachloride, benzene and dioxane carried out by American authors[22] have shown that, in dioxane, no ionization of hydrogen chloride takes place. The authors assume a hydrogen bond between the oxygen atoms of dioxane and the hydrogen atoms of hydrogen chloride[23].

As shown by the experiments above, a nearly immediate change in color of CV takes place if HCl is led into a solution of CV in toluene. With dioxane as a solvent, however, it takes a certain time before the blue of CV turns to yellow. The same is true if CV and dioxane are taken in nearly equal quantities. If 20 mg. of CV is dissolved in 10 cc. of monochlorobenzene, a certain amount of a solution of HCl in benzene has to be added to obtain the yellow color. If 20

mg. of dioxane is added to the solution of CV in monochlorobenzene, more HCl has to be added to observe the same yellow color. This means that a stronger interaction exists between dioxane and hydrogen chloride than between hydrogen chloride and CV; hence the bond O - - - - H in dioxane—HCl is stronger than the N—H bond in CV—HCl. The conclusion may be reached that in the coördinate complexes of CV with HCl, HBr, and HF, the bonds between the hydrogen atoms of these hydrogen halides and the nitrogen atoms in CV are hydrogen bonds, which corresponds to an analogous assumption in the case of alkyl olefins and hydrogen chloride[10].

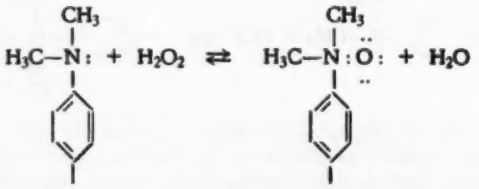
HALOGENS

If a dilute solution of chlorine or bromine in carbon tetrachloride is added to a blue solution of CV in monochlorobenzene, the color changes to yellow. On heating, the blue reappears, but decoloration of the solution soon takes place, probably because of radical attack.

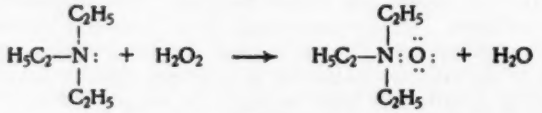
The addition of bromine to a double bond is assumed to proceed through a polar reaction mechanism. The reaction between chlorine and alkyl olefins has been believed to belong to the radical type. Recently, however, the suggestion has been made that chlorine may attack alkyl olefins in a polar way[24], which agrees with our experiments with CV.

OXYGEN AND SULFUR

If a few drops of a solution of CV in water are added to a few cc. of a 60 per cent hydrogen peroxide solution, a change from blue to yellow is observed. This may be explained by the fact that an oxygen atom adds to the nitrogen atoms of CV:



In support of this assumption the results of the experiments carried out by Shanley and Greenspan may be mentioned[25]. These authors investigated the reaction between amines and 90 per cent hydrogen peroxide solutions. In the case of triethylamine, triethylamine oxide was formed:



Heating the yellow solution of CV-oxygen complex causes a change to blue again, and, on cooling, the yellow reappears. However, rapid decoloration of the solution takes place, probably because hydrogen peroxide attacks CV in an irreversible way too.

Since it has been shown that polar agents cause a reversible shift in CV from blue to yellow, it may be assumed that the formation of an aminoxide of CV is a

polar reaction. We presume that an oxygen atom bearing a sextet acts as an acceptor, which probably involves the fact that hydrogen peroxide in its transition state has the branched structure $H_2O{:}\ddot{O}{:}$

If a finely powdered mixture of CV and sulfur is gently heated in a test-tube, a yellow sublimate settles on the cooler parts of the wall of the tube. This yellow compound turns blue on gentle heating, but on cooling the yellow compound is formed again. Sulfur monochloride (S_2CL_2) shows the same reaction when toluene is the solvent. Concerning the first reaction, we may say that sulfur, as might be expected from its strong coördination capacity, tends to react in straight chains of from one to six sulfur atoms, doubtless derived from the thermal scission[26] of originally cyclic S6 and S8. The sulfur analog of the amine oxide of CV may be described as shown in Figure 4.

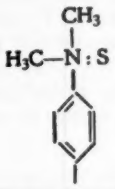


FIG. 4.

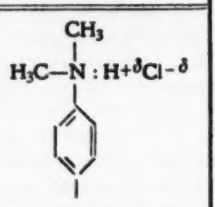
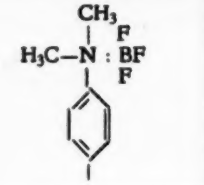
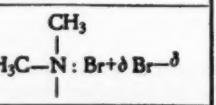
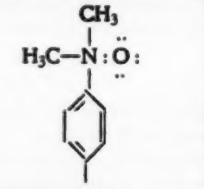
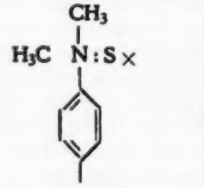
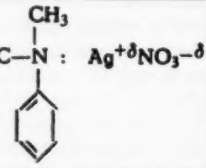
In the case of sulfur monochloride, we may assume that this compound is able to react in its branched structure. Analogous to what we have said concerning hydrogen peroxide, the assumption may be made that one sulfur atom is coördinatively bound, which atom is able to add to the nitrogen atoms of CV.

SILVER NITRATE

Since it is known from the experiments of Lucas[10] and Lewis[14] that silver nitrate and silver perchlorate are acceptor molecules and form coördinate complexes with donor olefins, it was of interest to investigate the complex formation with CV. Lewis has already shown that silver perchlorate gives a yellow color with CV in benzene solution. Our experiments revealed that silver nitrate does not cause a change from blue to yellow in CV with benzene as a solvent, which may be ascribed to the fact that this silver salt is practically insoluble in benzene. In nitroethane, which dissolves silver nitrate, no change in color was observed. However, in liquid sulfur dioxide, silver nitrate gave the yellow of CV, undoubtedly due to the formation of a CV-silver nitrate complex. At first sight it may be said that a solvent with a high dielectric constant is necessary for the formation of a complex. A medium of high dielectric constant induces a more ionic character of the silver atom in the silver nitrate molecule, which causes an increase in the acceptor properties of this atom (compare the addition of hydrogen chloride to olefins in liquid sulfur dioxide[27] with the hydrochlorination of olefins in ordinary organic solvents). In water or alcohol, although they are solvents with a high dielectric constant, the reaction between silver nitrate and CV does not proceed. These solvents, however, are relatively strong donors which compete with CV and, therefore, inhibit the reaction.

Since the coördinate complexes of CV with the chemicals mentioned above are difficult to handle, our experiments with CV have been confined to test-tube reactions. Distillation of the complex compounds cannot be carried out with-

Table II.

Chemical agent	Coordinate complex
Hydrogen halides	
Friedel en Crafts catalysts	
Halogen	
Oxygen	
Sulphur	
$AgNO_3$	

out decomposition; and crystallization is very difficult if not impossible, because the compounds have a very low solubility in nonpolar solvents and decompose in more polar solvents. If water, alcohol or ethyl acetate are added to, *e.g.*, the yellow CV—BF_3 complex, the blue of CV appears immediately. In general, those solvents which dissolve iodine with a brown color[2], decompose CV-complex compounds. If the donor properties of the solvent molecules are strong enough, CV can be replaced in its complex compounds by a solvent molecule.

The formulas of the complex compounds of CV and the reagents mentioned above are shown in Table II.

DISCUSSION

The surprising parallelism in the ability of donor olefins and CV to form complexes must be explained by assuming that both types of molecules have nearly the same donor properties. The influence of solvents on the rate of hydrochlorination of rubber and the formation of the CV—HCl complex is especially illuminating in this respect.

We may say that the following factors apparently balance the donor properties of CV and the double bond in rubber so that they finally become comparable:

1. the electron-withdrawing resonance effect;
2. the electron-releasing effect of the methyl group;
3. the effect caused by the different electronegative character of the carbon and nitrogen atom.

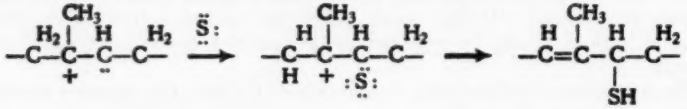
Further steric factors may play a role.

From all these facts it follows that a chemical reagent which gives a reversible shift in color from blue to yellow in CV will attack the double bond in rubber at the non-methylated carbon atom (polar reaction), and this forms the basis for our suggestion that CV may be used as a model substance for rubber and related olefins. Since the electronic structures of donor olefins and CV are involved, and not the molecular structure which usually dictates the choice of a model substance, we have called CV an electronic model substance.

In this paper the reverse picture is given of what is often found in the literature. For example, to differentiate between the reactivity of double bonds in olefins, the rate of reaction with perbenzoic acid has been used[28]. In this case the reactivities of a great many molecules containing double bonds are measured with respect to one reagent, *viz.*, perbenzoic acid. In our laboratory, investigations are under way on the formation of liquid complexes between silver salts and a series of olefins and other donor molecules[29]. The purpose of our experiments is to show that the action of many chemicals on the double bond in rubber and related olefins can be investigated by using a dye such as CV. Finally an application of the use of CV as an electronic model substance may be mentioned.

Of special interest is the fact that sulfur gives a coördinate complex with CV, which is of importance with regard to the vulcanization of rubber. In earlier literature we often find the assumption that, during vulcanization, sulfur reacts with the double bond in rubber. However, as far as we know, a formulation of this reaction has been given only by one author[30]. Farmer[31] has proposed a theory in which he assumes that under vulcanizing conditions sulfur reacts with the α-methylene groups in rubber in a radical reaction. Our experiments with CV, however, point in the direction of a polar reaction between rub-

ber and sulfur in the first stage of the vulcanization reaction. In agreement with the formulation given by Taft[24] concerning the reaction of olefins and chlorine, we are inclined to suggest that the following reaction scheme might describe the initial reaction between rubber and sulfur:



The sulfur atom is an acceptor strong enough to use the π-electrons for a bond between this atom and the non-methylated carbon atom of the double bond. The carbonium ion structure now formed stabilizes itself; and this can be done by a proton shift to the sulfur atom, thus giving rise to the formation of a thiol, which is assumed to be an important intermediate in modern vulcaniaztion theory.

SUMMARY

It is shown that triphenylmethyl dyes like crystal violet can be used as model substances for rubber and related olefins. Arguments are given in support of the assumption that agents which react with rubber and related olefins in a polar manner cause a reversible shift in color from blue to yellow with crystal violet, whereas a fading of the blue color of crystal violet (if alkaline or reducing agents are excluded) points to a radical reaction. Since the electronic structures of donor olefins and crystal violet are considered and not the molecular structure, as usually is done in the choice of a model substance, these dyes have been named *electronic model substances*. Though crystal violet, as an electronic model substance cannot be used for the study of the overall reactions, information can often be obtained concerning the first step in a reaction of rubber with a certain chemical agent by means of a simple test-tube reaction with crystal violet. It was pointed out that the π-electron availability at the non-methylated carbon atom of the double bond in rubber and at the nitrogen atoms in crystal violet is probably of the same order. As an application of crystal violet as an electronic model substance for rubber, a polar reaction between sulfur and rubber is suggested as the first step in vulcanization.

ACKNOWLEDGMENT

The author wishes to thank J. A. A. Ketelaar and G. Salomon for numerous helpful discussions, and is much indebted to the Rubber Foundation for permission to publish this paper.

REFERENCES

[1] Sidgwick, "The Electronic Theory of Valence," Oxford Univ. Press, 1929.
[2] Fairbrother, *J. Chem. Soc.* 1948, p. 1051.
[3] Benesi and Hildebrand, *J. Am. Chem. Soc.* 70, 2832 (1948).
[4] Conn, Kistiakowsky and Smith, *J. Am. Chem. Soc.* 60, 2764 (1938); Remick, "Electronic Interpretations of Organic Chemistry," New York, 1943, p. 229.
[5] Price, "Mechanisms of Reactions at Carbon—Carbon Double Bond," New York, 1946, Chap. 2.
[6] Scheibe and Pummerer, *Ber.* 60, 21, 73 (1927); Bateman and Koch, *J. Chem. Soc.* 1944, p. 600.
[7] Olefins in which the donor properties dominate are called donor olefins in this paper; *e.g.*, alkyl ethylenes.
[8] For convenience, the coördinate complexes are written with the acceptor molecule on the non-methylated carbon atom of the double bond. This would mean that this carbon atom is in the sp^2 state and the other in the sextet structure. It is now generally agreed that these structures are actually resonance hybrids (see Winstein and Lucas, *J. Am. Chem. Soc.* 60, 836 (1938); Walsh, *Nature* 159, 274 (1947).
[9] Waters, "Physical Aspects of Organic Chemistry," London, 1935, pp. 171–172.
[10] Whitmore, *Chem. Eng. News* 26, 668 (1948).

[11] Luder and Zuffanti, "The Electronic Theory of Acids and Bases," New York, 1946, p. 127; Kettelaar, "De Chemische Binding," Elsevier Publishing Co., 1947.
[12] Swern, *J. Am. Chem. Soc.* **69**, 1692 (1947).
[13] Winstein and Lucas, *J. Am. Chem. Soc.* **60**, 836 (1938).
[14] Rosenstein and Adams, *J. Am. Chem. Soc.* **36**, 1452 (1914).
[15] Meyer, *Ber.* **41**, 2568 (1908); Lewis, *J. Franklin Inst.* 1938, p. 306.
[16] Wieland and Maier, *Ber.* **64**, 1205 (1931).
[17] Iwamoto, *Chem. Zentr.* 1936, I, 533.
[18] Hunter and Yoke, *J. Am. Chem. Soc.* **55**, 1248 (1933); Bright and Fernelius, *J. Am. Chem. Soc.* **55**, 735 (1943).
[19] Lewis and Calvin, *Chem. Revs.* **25**, 273 (1939).
[20] Van Veersen, *Proc. 2nd Rubber Tech. Conf. London*, 1948, p. 87.
[21] Salomon, Koningsberger, and Ultée, *Proc. 2nd Rubber Tech. Conf. London*, 1948, p. 106.
[22] Werth, Hobbs and Groese, *J. Am. Chem. Soc.* **70**, 805 (1948).
[23] O'Brien, *J. Am. Chem. Soc.* **62**, 1109 (1940); Syrkin and Anisimova, *Doklady Akad. Nauk. S.S.S.R.* **59**, 1457 (1948).
[24] Taft, *J. Am. Chem. Soc.* **70**, 3364 (1948).
[25] Shanley and Greenspan, *Ind. Eng. Chem.* **39**, 1536 (1947).
[26] Farmer and Shipley, *J. Polymer Sci.* **1**, 293 (1946); Bloomfield, *J. Polymer Sci.* **1**, 312 (1946).
[27] U. S. patent 2,459,423 (1949).
[28] Kolthoff and coworkers, *J. Polymer Sci.* **2**, 199, 206 (1947).
[29] Salomon and Koningsberger, *J. Polymer Sci.* **2**, 522 (1947); Salomon, G., private communication.
[30] Williams, *Ind. Eng. Chem.* **39**, 901 (1947); *India Rubber World* **117**, 69 (1947).
[31] Farmer, RUBBER CHEM. & TECHNOL. **15**, 765 (1942).

BIREFRINGENCE OF RUBBERS *

D. W. SAUNDERS

BRITISH RUBBER PRODUCERS' RESEARCH ASSOCIATION, WELWYN GARDEN CITY, HERTFORDSHIRE, ENGLAND

It has been shown, both theoretically[1] and experimentally[2], that in simple elongation of a sample of pure-gum vulcanizate, an approximately linear relationship between the tensile stress t and the birefringence $(n_1 - n_2)$ obtains, provided the strain is not sufficiently large to produce crystallization. We may write: $(n_1 - n_2) = Ct$, where C, the constant of proportionality, is termed the *stress coefficient*, and is theoretically independent of the degree of cross-linking (vulcanization) of the vulcanizate, and should be identical for all pure rubbers.

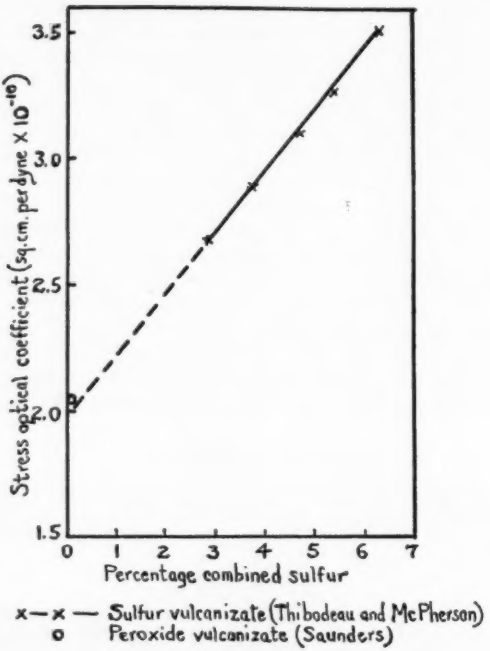


FIG. 1.

Thibodeau and McPherson[3] have shown that the stress-optical coefficient depends on the type of vulcanization. In particular, for gum vulcanized by means of sulfur without accelerators, but in the presence of stearic acid and zinc oxide, they found the stress-optical coefficient to depend linearly on the per-

* Reprinted from *Nature*, Vol. 165, page 360, March 4, 1950.

centage of combined sulfur. This dependence on the degree of vulcanization suggests that the sulfur is modifying either the polarizability or the stiffness of the molecular chains of the network. An extrapolation of the linear relation to zero combined-sulfur content has been used by Treloar as a measure of the birefringence of the actual molecular network.

Recently a vulcanized rubber has been produced which is free from all additions to the rubber; particularly it is free from sulfur. The vulcanization is achieved by a peroxide reaction[4], and all the byproducts can be removed, leaving a pure hydrocarbon vulcanizate. It is interesting to determine the stress-optical coefficient for this material and to compare it with the results of Thibodeau and McPherson.

The birefringence of a thin strip of the peroxide vulcanizate elongated under a known load was measured by means of Nicol prisms and a Babinet compensator. The relation between the stress and birefringence was found to be linear and reversible up to strains of about 100 per cent, and the stress-optical coefficient was 2.05×10^{-10} sq. cm. per dyne. This compares very well with the value obtained by extrapolating the results of Thibodeau and McPherson to zero combined-sulfur content.

REFERENCES

[1] Kuhn and Grün, *Kolloid-Z.* **101**, 248 (1942).
[2] Thibodeau and McPherson, *Bur. Standards J. Research* 13, 887 (1934); RUBBER CHEM. & TECHNOL. **8**, 183 (1935); Treloar, *Trans. Faraday Soc.* **43**, 284 (1947).
[3] Thibodeau and McPherson, *Bur. Standards J. Research* 13, 887 (1934); RUBBER CHEM. & TECHNOL. **8**, 183 (1935).
[4] Farmer and Moore, unpublished work; but see Gee, *Trans. Inst. Rubber Ind.* **25**, 88 (1949).

PARTIALLY CHLORINATED DERIVATIVES OF RUBBER *

D. E. Woods

Research Department, General Chemicals Division, Imperial Chemical Industries, Ltd., Widnes, England

INTRODUCTION

An immense volume of work has been done on fully chlorinated crepe rubber containing approximately 65 per cent of combined chlorine[1], but very little has been published concerning partially chlorinated derivatives of rubber. It was found that partially chlorinated rubbers containing from 30–60 per cent of combined chlorine were cream colored powders resembling fully chlorinated rubber in appearance, but differing from it in being unstable to heat and light. They decomposed rapidly at 100° C, but more slowly at room temperature, darkening and becoming hard and brittle.

Derivatives containing from 1–17 per cent chlorine were prepared in order to produce a derivative which would still be rubberlike, but would possess good oil and flame resistance.

It was found, as would be expected, that hardness increased with increasing chlorine content. Partially chlorinated rubbers containing 13 per cent or more chlorine gave hard vulcanizates resembling hard vulcanized rubber, and most of the work described was carried out with a product containing 10 per cent.

EXPERIMENTAL

PREPARATION, VULCANIZATION AND PHYSICAL TESTING

P.C.R. Vulcanizates[2]

Preparation

Preliminary experiments showed that the following procedure gave a satisfactory product.

Crepe rubber was dissolved in carbon tetrachloride to give a 2.5 per cent solution (wt./wt.) in an enamel or lead-lined mild steel stirred vessel. Gaseous chlorine was passed into the stirred solution at room temperature until the rubber had attained the required degree of chlorination, after which the solution was freed from dissolved HCl and chlorine by air blowing. The solvent was removed by steam distillation and the product dried on warm masticating rolls, 2 per cent of phenyl-α-naphthylamine being incorporated as antioxidant. The product was a brownish elastic mass very similar to lightly vulcanized crepe rubber.

Vulcanization and physical testing

It was found that partially chlorinated rubber could be readily vulcanized by the hot or cold method; when it contained 15 per cent or more of chlorine, the addition of vulcanizing agents was unnecessary. Fillers, metallic oxides,

* Reprinted from the *Journal of the Society of Chemical Industry*, Vol. 68, pages 343–348 (1949).

sulfur, and accelerator were generally added to improve the mechanical properties.

Method

Compounding was carried out in the usual way on mixing rolls. The time of mixing was kept as short as possible to avoid degradation of the rubber; it usually occupied from 10 to 20 minutes. The carbon black used was Kosmos T. The magnesium oxide was extra-light calcined, and the zinc oxide finely divided. The sulfur was the precipitated form. Hot vulcanization was carried out in a steam-heated press at 141° C.

For cold vulcanization, the rubber sheet was immersed in 3 per cent sulfur monochloride in carbon tetrachloride for 10 minutes at 25° C; then dried in air at room temperature.

Results

Products containing various percentages of chlorine

The vulcanizates varied from soft extensible rubberlike substances to hard brittle substances resembling ebonite as the percentage of chlorine in the partially chlorinated rubber was increased from 1 to 17 per cent. Typical results are shown in Table I.

TABLE I

VULCANIZATES FROM PARTIALLY CHLORINATED RUBBER CONTAINING VARIOUS PERCENTAGES OF CHLORINE

100 g. of crepe or partially chlorinated rubber with 50 g. carbon black, 4 g. stearic acid, 10 g. zinc oxide, 3 g. sulfur and 1 g. diphenylguanidine, vulcanized for 45 minutes at 141° C.

Sample No.	Chlorine content (%)	Hardness
67	Nil (crepe)	Very soft and pliable
66	2	Soft and pliable
64	4	Soft and pliable
57	6	Soft and pliable
54	9	Fairly soft and pliable
59	10	Fairly soft and pliable
60	11	Fairly soft and pliable
55	13	Fairly stiff
58	15	Hard
65	17	Very hard and brittle

The tensile strengths and percentage elongations at the break-point of these vulcanizates were measured using a Goodbrand cloth testing machine (3/340) 3–7 days after vulcanization. Tensile strength and elongation at the break-point decreased progressively with increasing chlorine content.

Partially chlorinated rubber containing 10 per cent chlorine

Further experiments were limited to a product containing 10 per cent of chlorine. Soft vulcanizates were obtained in every case.

In all these experiments the weight of carbon used was 50 per cent of that of partially chlorinated rubber, since preliminary experiments had shown that tensile strength increased with increase of carbon up to about 75 per cent, while elongation at the break-point decreased; this decrease, however, was not appreciable with mixes containing up to 50 per cent of added carbon.

The incorporation of as little as 0.5 per cent sulfur alone increased the tensile

strength and extensibility of the product. When both sulfur and diphenylguanidine were included, substitution of magnesium oxide for zinc oxide not only increased the elongation at the break-point but also the tensile strength. These increased with increase of magnesium oxide up to at least 10 per cent. Tensile strength and elongation also increased with increase of the amount of sulfur up to at least 10 per cent.

Vulcanizates with tensile strength 1420 and 2050 lb. per sq. in. and elongation of 200 and 300 per cent, respectively, were obtained using 10 per cent of MgO. These values, of course, are inferior to those of typical soft-vulcanized crepe rubber.

Variations of the proportions of zinc oxide, magnesia, and sulfur were tried in conjunction with short times of vulcanization, but the best result was tensile strength 1580 lb. per sq. in. and elongation 280 per cent. Incorporation of small amounts of stearic acid or chlorinated paraffin rendered the vulcanizates softer but decreased the tensile strength (Table II).

Partially Chlorinated Rubber—Chlorinated Rubber Vulcanizates

Incorporation of fully chlorinated rubber (64–65 per cent chlorine) was next tried to increase the total chlorine content; hence oil and flame resistance, of partially chlorinated rubber. Unlike rubber itself and fully chlorinated rubber, which are incompatible except in the presence of a plasticizer, partially and fully chlorinated rubbers gave homogeneous mixtures. The type of product varied, of course, with variation of the proportions of the two solids; thus a solid ratio 1:5 (partially chlorinated/fully chlorinated rubber) gave a brittle solid, while a ratio 1:2 gave a slightly elastic, tough material which could be rolled out into thin sheets, and a ratio 2:1 gave a much softer and more flexible sheet, not much stiffer than the original partially chlorinated rubber.

Preparation

A carbon tetrachloride solution of fully chlorinated rubber was added to the carbon tetrachloride solution of partially chlorinated rubber before distillation. After removal of the solvent by distillation, the product was dried on masticating rolls and 2 per cent of phenyl-α-naphthylamine added as antioxidant. In some preparations, powdered fully chlorinated rubber was incorporated with the solid partially chlorinated rubber on masticating rolls as a filler.

Vulcanization and physical testing

Vulcanizates were much softer and more flexible than those from partially chlorinated rubber containing the same amount of chlorine, *e.g.*, a product containing 38 per cent total chlorine was quite flexible and had an elongation at the break-point of 40 per cent.

Results

Mixtures from partially chlorinated rubber containing various percentages of chlorine.

From tensile strength and elongation tests on cold vulcanizates without the addition of fillers and accelerators, it was found that tensile strength increased with:

(1) Increase of chlorine in the partially chlorinated rubber.

(2) Increase of percentage fully chlorinated rubber in the mixture, while elongation decreased with increase of either of these two factors (Table III).

TABLE II

VULCANIZATES FROM PARTIALLY CHLORINATED RUBBER (10 PER CENT CHLORINE), ZINC OXIDE, MAGNESIUM OXIDE, CARBON BLACK, SULFUR, AND DIPHENYLGUANIDINE (1 G.). TEMPERATURE 141° C

Sample No.	P.C.R. (g.)	Carbon black (g.)	ZnO (g.)	MgO (g.)	Sulfur (g.)	Time (min.)	Tensile strength (lb./sq. in.)	Elongation at break-point (%)
138	100	50	—	5	0.5	45	500	180
146	100	50	—	5	2	45	610	130
162	100	50	10	—	2	30	660	25
162A	100	50	10	—	2	45	750	20
162B	100	50	10	—	2	90	660	17
161	100	50	6	4	2	30	730	110
161A	100	50	6	4	2	45	880	60
161B	100	50	6	4	2	90	1040	45
160	100	50	4	6	2	30	920	110
160A	100	50	4	6	2	45	890	75
160B	100	50	4	6	2	90	1020	60
159	100	50	2	8	2	30	880	130
159A	100	50	2	8	2	45	800	165
159B	100	50	2	8	2	90	1000	65
173	100	50	—	10	2	30	930	160
173A	100	50	—	10	2	45	690	85
173B	100	50	—	10	2	90	600	40
167	100	50	10	—	5	30	860	30
167A	100	50	10	—	5	45	890	20
167B	100	50	10	—	5	90	810	10
166	100	60	6	4	5	30	1140	90
166A	100	50	6	4	5	45	920	75
166B	100	50	6	4	5	90	1180	55
165	100	50	4	6	5	30	1060	65
165A	100	50	4	6	5	45	1120	80
165B	100	50	4	6	5	90	1170	85
164	100	50	2	8	5	30	990	95
164A	100	50	2	8	5	45	1260	75
164B	100	50	2	8	5	90	1040	80
163	100	50	—	10	5	30	1790	195
163A	100	50	—	10	5	45	1550	105
163B	100	50	—	10	5	90	1020	80
168	100	50	10	—	10	30	470	20
168A	100	50	10	—	10	45	480	20
168B	100	50	10	—	10	90	580	10
169	100	50	6	4	10	30	800	90
169A	100	50	6	4	10	45	880	70
169B	100	50	6	4	10	90	1280	65
170	100	50	4	6	10	30	875	120
170A	100	50	4	6	10	45	960	100
170B	100	50	4	6	10	90	1010	90

TABLE II—(*Continued*)

Sample No.	P.C.R. (g.)	Carbon black (g.)	ZnO (g.)	MgO (g.)	Sulfur (g.)	Time (min.)	Tensile strength (lb./sq. in.)	Elongation at break-point (%)
171	100	50	2	8	10	30	1100	125
171A	100	50	2	8	10	45	900	80
171B	100	50	2	8	10	90	1120	85
172	100	50	—	10	10	30	1300	240
172A	100	50	—	10	10	45	1130	175
172B	100	50	—	10	10	90	970	150
176	100	50	—	10	5	15	1420	200
177	100	50	—	10	10	15	2050	300
194	100	50	—	15	10	10	1380	300
194A	100	50	—	15	10	20	1580	280
194B	100	50	—	15	10	30	1830	175
196	100	50	—	10	15	10	1160	220
196A	100	50	—	10	15	20	1480	210
196B	100	50	—	10	15	30	1400	180
192	100	50	—	15	15	5	1170	300
192A	100	50	—	15	15	15	1620	210
192B	100	50	—	15	15	30	1300	120
			Stearic acid					
200	100	50	5	10	10	15	900	280
200A	100	50	5	10	10	30	1220	200
200B	100	50	5	10	10	45	1170	160
			Chlorinated paraffin wax					
195	100	50	10	10	10	15	1570	290
195A	100	50	10	10	10	40	1320	165
195B	100	50	10	10	10	45	1270	96
203	100	50	35	10	10	15	230	270
203A	100	50	35	10	10	30	820	250
203B	100	50	35	10	10	45	800	160

Mixtures from partially chlorinated rubber containing 10 per cent chlorine.

Table IV gives the mixes used in and results of hot and cold vulcanization with 10 per cent chlorine partially chlorinated rubber/fully chlorinated rubber mixtures. In these experiments addition of carbon, magnesium oxide, sulfur, and diphenylguanidine was tried, as before. With cold or hot vulcanization, tensile strength increased with increase of fully chlorinated rubber content, while elongation decreased.

CHEMICAL, OIL AND FLAME RESISTANCE

Electrical Properties

Chemical and Heat Resistance

Method

Specimens of equal size from vulcanizates of partially chlorinated rubber containing various amounts of chlorine up to 17 per cent were subjected to the

TABLE III

PARTIALLY CHLORINATED RUBBER/FULLY CHLORINATED RUBBER VULCANIZATES FROM PARTIALLY CHLORINATED RUBBER OF VARIOUS CHLORINE CONTENTS

Sample No.	P.C.R. (% chlorine)	Mixture P.C.R. %	Mixture C.R. %	Time (min.)	Temp. (° C)	Tensile strength (lb./sq. in.)	Elongation at break-point (%)
141B	2	67	33	10	25	200	110
141A	2	50	50	10	25	750	90
141	2	33	67	10	25	930	20
140B	4	67	33	10	25	470	75
140A	4	50	50	10	25	500	80
140	4	33	67	10	25	1050	10
144	4	20	80	10	25	1150	5
142B	10	67	33	10	25	900	85
142A	10	50	50	10	25	1050	40
147	10	40	60	10	25	850	20
142	10	33	67	10	25	1130	15
145	10	20	80	10	25	880	5
149	14	50	50	10	25	1340	25
148	14	50	50	45	141	370	Nil
181C	14	40	60	10	25	1640	2
143A	15	67	33	10	25	1020	80
128	15	50	50	10	25	1650	50
143	15	33	67	10	25	(800)	15

TABLE IV

PARTIALLY CHLORINATED RUBBER/FULLY CHLORINATED RUBBER VULCANIZATES FROM MIXTURES MADE UP ON MASTICATING ROLLS (10% CHLORINE P.C.R.)

Sample No.	Mixture P.C.R. (g.)	Mixture F.C.R. (g.)	Carbon balck (g.)	MgO (g.)	Sulfur (g.)	D.P.G. (g.)	Time (min.)	Temp. (° C)	Tensile strength (lb./sq. in.)	Elongation at break-point (%)
184	80	20	—	—	—	—	10	25	620	105
186A	80	20	20	—	8	0.8	10	25	650	120
190C	80	20	20	8	4	0.8	10	25	840	110
186	80	20	20	—	8	0.8	30	60	60	54
158	80	20	—	—	8	0.8	60	60	Soft and sticky	
187	80	20	20	8	4	0.8	240	70	300	230
187B	80	20	20	8	4	0.8	600	70	680	300
190	80	20	20	8	4	1	360	65	320	140
190A	80	20	20	8	4	1	600	65	570	200
190B	80	20	20	8	4	1	120	100	700	180
189A	70	30	—	—	—	—	10	25	380	70
189	70	30	—	—	—	—	360	65	90	80
189B	70	30	—	—	—	—	600	70	150	75
191B	70	30	18	7	3.5	0.7	10	25	850	60
191	70	30	18	7	3.5	0.7	240	100	840	145
191C	70	30	18	7	3.5	0.7	600	100	220	95
191A	70	30	18	7	3.5	0.7	30	141	1060	65
191D	70	30	18	7	3.5	0.7	60	141	900	45
193C	60	40	—	6	6	0.6	10	25	(240)	60
193	60	40	—	6	6	0.6	15	141	610	100
193A	60	40	—	6	6	0.6	30	141	600	55
193B	60	40	—	6	6	0.6	45	141	670	65

action of: (1) 10% HCl. (2) 32% HCl. (3) 20% NaOH. (4) Brine saturated with chlorine. (5) Heat at 60° C and (6) Heat at 100° C for 15 days.

A control specimen of crepe similarly compounded and vulcanized was included in each series.

Results

The results showed that in the case of hydrochloric acid, partially chlorinated rubber was less resistant than crepe, absorption reaching a maximum and then decreasing with increasing chlorine content. With caustic soda, resistance was also less than that of crepe. The resistance to chlorine-saturated brine increased with increasing chlorine content. The results at 60° and 100° C were irregular.

Oil Resistance

Method

Specimens of equal size from vulcanizates of partially chlorinated rubber containing various amounts of chlorine up to 17 per cent, and from a series of partially chlorinated rubber/fully chlorinated rubber vulcanizates, together with a control specimen of vulcanized crepe, were immersed at room temperature in: (1) motor spirit; (2) turpentine; (3) diesel oil; and (4) a spindle oil.

Results

Partially chlorinated rubber

The results (Table V) showed, as would be expected, that the resistance to each solvent increased with increasing chlorine content until, at 17 per cent chlorine, oil absorption was almost negligible compared with that of vulcanized crepe.

TABLE V

OIL RESISTANCE OF PARTIALLY CHLORINATED RUBBER VULCANIZATES
(72 HOURS IMMERSION)

Sample No.	Chlorine content of P.C.R. (%)	Motor spirit gain (%)	Turpentine gain (%)	Diesel oil gain (%)	Spindle oil gain (%)
			A.		
67	Nil	374	560	235	39
66	2	316	438	215	41
64	4	262	360	208	44
57	6	106	112	123	26
59	10	90	102	66	14
60	11	112	134	62	4
55	13	83	50	8	0.6
58	15	58	16	2	Nil
44	17	22	Nil	0.5	0.1
			B.		
178	Nil	616	882	520	260
176	10	207	270	160	139
177	10	186	235	133	64
179	10	136	185	105	39

Partially chlorinated rubber/fully chlorinated rubber

For these vulcanizates, oil resistance in general increased with increase in the proportion of fully chlorinated rubber; the percentage of chlorine in the partially chlorinated rubber had a much smaller effect. In this series of experiments the increase in weight was calculated on the total weight of the specimen. In all cases the increase in weight of the chlorinated rubber vulcanizate was much less than that of vulcanized crepe (Table VI).

TABLE VI

OIL RESISTANCE OF PARTIALLY CHLORINATED RUBBER/FULLY CHLORINATED RUBBER VULCANIZATES (72 HOURS' IMMERSION)

Sample No.	Chlorine content of P.C.R. (%)	P.C.R. (%)	F.C.R. (%)	Motor spirit gain (%)	Turpentein gain (%)	Diesel oil gain (%)	Spindle oil gain (%)
67	Nil	—	—	220	305	140	22
141B	2	67	33	>100	>120	95	>6
141A	2	50	50	102	122	53	6.0
141	2	33	67	52	84	19	1.0
140B	4	67	33	122	148	72	10
140A	4	50	50	133	210	67	4.4
140	4	33	67	59	68	5.6	4.4
144	4	20	80	31	45	1	0.1
142B	10	67	33	118	156	65	2.7
142A	10	50	50	89	75	39	0.6
142	10	33	67	69	88	23	0.7
145	10	20	80	40	86	11	3.0
143A	15	67	33	97	136	52	2.8
128	15	50	50	32	45	13	0.6
143	15	33	67	89	114	20	0.2

Flame Resistance

Several vulcanizates were subjected to the Post Office flame test for cables to find the best mixes for flame resistance (P.O. Specification No. 574).

Results

Partially chlorinated rubber vulcanizates

The flame resistance was increased by increasing:

(1) the percentage of chlorine in the partially chlorinated rubber;
(2) the proportions of nonrubber components;
(3) the sulfur; and
(4) the time and temperature of vulcanization;

i.e., it was increased by decreasing the proportion of rubber hydrocarbon present and increasing the degree of vulcanization.

In general, vulcanizates from partially chlorinated rubber containing 17, 15, and 13 per cent of chlorine passed, unless the values of (2), (3) and (4) were low, while those from partially chlorinated rubber containing 10 per cent of chlorine failed.

Attempts to render 10 per cent chlorine vulcanizates flameproof by increasing the amounts of carbon and magnesium oxide in the mix and also by incorporating chlorinated paraffin wax (46 per cent chlorine) were successful only in the latter case.

TABLE VIIA

ELECTRICAL PROPERTIES OF PARTIALLY CHLORINATED RUBBER VULCANIZATES

Sample No.	Chlorine content of P.C.R. (%)	Breakdown voltage (volts/mil; 50 cycles/second; room temperature)	Volume resistivity after 10 minutes electrification (ohms/cm³; room temperature)
176	10	40	1×10^{10}
177	10	35	2×10^{9}
200	10	44	4×10^{10}
200A	10	40	5×10^{10}
201 (25%	10	90	1×10^{11}
201A carbon	10	120	8×10^{10}
201B black)	10	120	3×10^{11}
203A	10	20	4×10^{9}
203B	10	30	4×10^{9}

Partially chlorinated rubber/fully chlorinated rubber vulcanizates

When the percentage of fully chlorinated rubber had reached a certain value (33 per cent incorporated in solution; 40 per cent added on masticating rolls) cold vulcanizates passed the test. The hot vulcanizates just failed, however, in spite of the fact that the original chlorinated rubber mixtures, the unvulcanized mixes, and the cold vulcanizates passed. This may have been due to volatilization at 141° C of residual carbon tetrachloride in the fully chlorinated rubber or to slight decomposition of the latter. Hot vulcanizates from a mixture of 14 per cent partially chlorinated rubber containing 60 per cent of fully chlorinated rubber passed the test.

TABLE VIIB

ELECTRICAL PROPERTIES OF PARTIALLY CHLORINATED RUBBER/FULLY CHLORINATED RUBBER VULCANIZATES

Sample No.	Chlorine content of P.C.R. (%)	P.C.R. (%)	F.C.R. (%)	Breakdown voltage (volts/mil.; 50 cycles/second; room temperature)	Volume resistivity after 10 minutes electrification (ohms/cm³; room temperature)	Permitivity (50 cycles/second; room temperature)	Power factor at 75% humidity (50 cycles/second; room temperature)
141A	2	50	50	310	1.7×10^{14}	2.6	0.071
140A	4	50	50	280	9.9×10^{13}	4.1	0.056
140	4	33	67	540	4.6×10^{14}	3.6	0.023
144	4	20	80	550	2.1×10^{14}	3.7	0.016
199A	10	70	30	300(A)	5.0×10^{14}	4.7	0.039
199C	10	70	30	250(A)	5.0×10^{15}	4.5	0.020
142B	10	67	33	540	4.6×10^{14}	3.6	0.023
198	10	65	35	240(A)	1.0×10^{15}	5.0	0.037
198B	10	65	35	200(A)	1.0×10^{15}	7.4	0.060
193C	10	60	40	500	7.0×10^{13}	5.5	0.019
197C	10	60	40	300(A)	1.0×10^{15}	4.6	0.025
204A	10	60	40	170(A)	2.0×10^{11}	—	—
204B	10	60	40	160(A)	9.0×10^{11}	—	—
204C	10	60	40	400(A)	1.0×10^{15}	4.7	0.018
142A	10	50	60	580	8.0×10^{14}	3.5	0.017
142	10	33	67	560	2.6×10^{14}	3.7	0.022
145	15	20	80	350	7.0×10^{14}	4.0	0.018
143A	10	67	33	470	2.0×10^{14}	3.9	0.029
143	15	33	67	460	3.2×10^{14}	3.8	0.029

The specimens had irregular surfaces which would tend to bring the breakdown voltages to lower values than would otherwise be the case.

Electrical Properties

Partially chlorinated rubber vulcanizates

The values of various electrical properties were determined on the vulcanizates possessing the best mechanical properties and on certain vulcanizates containing 25 per cent only of added carbon.

The results (Table VIIa) show the beneficial effect, on breakdown voltage and resistivity, of reducing the amount of carbon and the deleterious effect of chlorinated paraffin wax (203A and B).

Partially chlorinated rubber/fully chlorinated rubber vulcanizates

Most of the specimens were satisfactory with respect to all the electrical properties determined. The low results on specimens 204A and B again show the deleterious effect of carbon in hot vulcanizates (Table VIIb).

Corresponding values of soft vulcanized crepe rubber are:

(1) Volume resistivity 10^{13}–10^{16} ohms per cc.;
(2) Break-down voltage 50–750 volts per mil;
(3) Power factor 0.014–0.05;
(4) Permittivity 2.7–3.8.

CONCLUSIONS

1. The oil, flame, and chlorine resistance of partially chlorinated rubber increase with increasing chlorine content.

2. The tensile strength and elasticity decrease with increasing chlorine content.

3. Vulcanizates from partially chlorinated rubber containing 10 per cent of chlorine are sufficiently rubberlike and a tensile strength of 2000 lb. per sq. in. and an elongation at the break-point of 300 per cent can be obtained by compounding with carbon, magnesium oxide, sulfur, and diphenylguanidine.

4. They do not pass the Post Office flame test for cables, and their electrical properties are, in general, somewhat inferior to those of soft vulcanized crepe rubber.

5. Partially chlorinated rubber is compatible with fully chlorinated rubber.

6. Vulcanizates from mixtures of 67–60 per cent of partially chlorinated rubber, containing 10 per cent chlorine, with 33–40 per cent of fully chlorinated rubber have tensile strengths of the order 900 lb. per sq. in. and elongations of the order 100 per cent. They pass the Post Office flame test, and have electrical properties equal to those of vulcanized crepe rubber; hence they should prove fairly satisfactory as electric cable sheathings.

SUMMARY

Chlorinated rubbers containing from 1 to 17 per cent of chlorine were prepared by direct chlorination, at ordinary temperature, of crepe rubber dissolved in carbon tetrachloride. These products retain, to a greater or lesser degree, rubberlike properties, and are capable of hot or cold vulcanization with or without the addition of vulcanizing agents. The resulting vulcanizates are considerably more resistant to the swelling action of solvents, and also to the action of chlorine, than corresponding products prepared from crepe rubber. The resistance to swelling agents increased with increase in combined chlorine content; tensile strength and elasticity, however, decreased with increasing chlorine content. As expected, hardness increased with increase of chlorine

content, and vulcanizates from derivatives containing more than 10 per cent combined chlorine were not sufficiently rubberlike to warrant many experiments. Fully chlorinated rubber was compatible with partially chlorinated rubber, and addition of the former was necessary for vulcanizates to pass the Post Office flame test for cables.

ACKNOWLEDGMENT

The thanks of the author are due to the Directors of Imperial Chemical Industries, Ltd. (General Chemicals Division) for permission to publish this paper.

REFERENCES

[1] Smith, *Oil and Colour Trades J.* **88**, 1251 (1935); Baxter, *J. Soc. Chem. Ind.* **55**, 407 (1936); *Rev. Paint and Colour Varnish Manuf.* **57**, 205 (1937); Baxter and Moore, *J. Soc. Chem. Ind.* **57**, 327 (1938).

[2] Throughout this paper, P.C.R. designates partially chlorinated rubber.

THE PREPARATION OF CYCLIZED RUBBER FROM NATURAL-RUBBER LATEX *

G. J. VAN VEERSEN

RUBBER FOUNDATION, DELFT, HOLLAND

INTRODUCTION

The hydrochlorination of rubber in the form of latex[1] which has been stabilized by surface-active agents, such as Emulphor-O, or by cationic agents such as Fixanol, shows that hydrogen chloride molecules diffuse very easily into the latex globules. Accordingly it was to be expected that, by replacing hydrogen chloride gas by hydrogen fluoride gas, which is a cyclizing agent of rubber, a cyclized rubber[2] would be obtained. This line of reasoning was confirmed experimentally. As a result of an experimental study, it was proved that boron fluoride, BF_3 also, brings about cyclization of rubber in latex, and van Amerongen has already shown that sulfuric acid likewise can be used as a catalyst. Since sulfuric acid is much easier to handle than either hydrogen fluoride or boron fluoride, it was used in most of the experiments in the present work.

CYCLIZATION OF RUBBER IN THE FORM OF LATEX BY MEANS OF SULFURIC ACID

To 134 grams of latex containing 58 per cent of dry rubber, and stabilized with 1.5 per cent of Emulphor-O, was added 161 grams of concentrated sulfuric acid to a point where the serum of the latex contained 75 per cent by weight of the acid. After heating for 6 hours at 80° C, the reaction mixture was diluted with 3 times its volume of water. The dispersion thus obtained was filtered. After washing and drying, the cyclized rubber showed a polyisoprene unsaturation[3] corresponding to 26.

To find out more about the rate of the cyclization process in the latex medium, the reaction was carried out at several different temperatures. Latex containing 60 per cent of dry rubber was stabilized with 2 per cent of Emulphor-O; concentrated sulfuric acid was then added in such proportion that the serum contained 75 per cent by weight of the acid. The mixture was then heated at 70°, 80°, 90°, and 100° C, respectively. During the reaction, samples were removed for the purpose of determining the polyisoprene unsaturation. This factor was chosen as a measure of the degree of unsaturation.

The results of these measurements are shown in Figure 1.

As judged by the data in Figure 1, the higher the temperature, the greater is the rate of the reaction, at least within the range of temperatures studied.

From a different point of view, it was interesting to study the influence of the concentration of sulfuric acid and of the temperature on the degree of cyclization and, above all, to determine the minimum effective proportion of sulfuric acid. To this end, 30-cc. samples of latex were stabilized with 2 per cent of Emulphor-O; to these samples were added various proportions of

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Revue Générale du Caoutchouc*, Vol. 27, No. 8, pages 473–474, August 1950. This paper is Communication No. 93 of the Rubber Foundation, Delft, Holland.

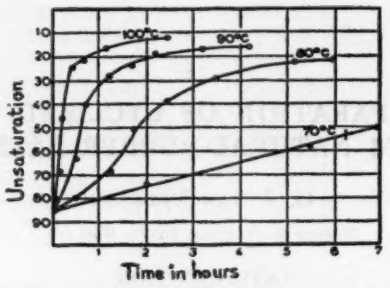


FIG. 1.—Cyclization, at different temperatures, of rubber in latex containing 75 per cent by weight of sulfuric acid.

sulfuric acid, and the mixtures were heated for seventeen hours at different temperatures.

Subsequent dilution of the reaction mixtures with water gave products which were filtered, washed, and analyzed for their degrees of unsaturation. The degree of unsaturation was again chosen as a measure of the degree of cyclization. Figure 2 shows the results obtained.

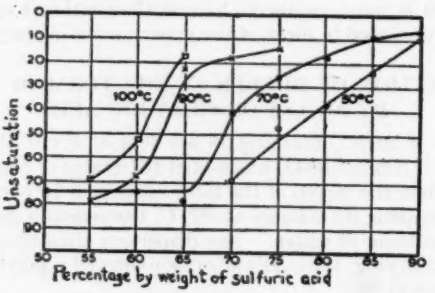


FIG. 2.—Influence of the concentration of sulfuric acid and of the temperature on the cyclization of rubber in the form of latex.

The data in Figure 2 show that the temperature and the concentration of the sulfuric acid both govern the degree of polymerization. Below a concentration of 60 per cent by weight of sulfuric acid, there was practically no cyclization, even at 100° C. It should be pointed out that the method of measurement used in the present work gave for rubber[2] an unsaturation value of 87, and that values lying between 70 and 87 indicate that there had been practically no cyclization.

Although this method of cyclization requires a quantity of rubber greater than that required for the cyclization of solid rubber, it has the considerable advantage of yielding a cyclized rubber in the form of latex. It is, in fact, easy to prepare a fine dispersion of cyclized rubber if, after the sulfuric acid has been removed by filtering and washing, the still moist product is treated, in a ball mill, with the proper amount of water.

An application of such a cyclized-rubber latex will be described in a later communication.

REFERENCES

[1] Van Veersen, *2nd Rubber Technol. Conf. London*, 1948, p. 87; RUBBER CHEM. & TECHNOL. 23, 461 (1950).
[2] Van Veersen, "The structure of cyclized rubber," *Rec. trav. chim.*, in press.

POLAR RUBBERS AND THEIR APPLICATION AS ION EXCHANGERS *

PIERRE MASTAGLI

ORGANIC CHEMICAL LABORATORY, CATHOLIC INSTITUTE, PARIS, FRANCE

GEZA AUSTERWEIL

RESEARCH DEPARTMENT, PECHINEY CO., PARIS, FRANCE

AND

AZFIRI ZAFIRIADIS

ORGANIC CHEMICAL LABORATORY, CATHOLIC INSTITUTE, PARIS, FRANCE

INTRODUCTION

Most of the ion exchangers in current use are prepared in the form of synthetic resins by the condensation of aldehydes or of ketones with amines or substituted phenols and polymerization these condensation products.

However, resins prepared in this way have certain disadvantages, *e.g.*, their solubility, instability, and tendency to swell. As early as 1938, one of the present authors was able to show that it is possible to obtain ion exchangers by avoiding the condensation phase of the process through the introduction of polar groups directly into the macromolecules, which are, and which remain, insoluble even after the introduction of polar groups (wool, aminopolystyrene, azotized rubber, etc.)[1].

By eliminating the condensation phase, the —RCH(R')OH groups and consequently any steric hindrance[2] are avoided; hence, the stability and effectiveness of the products as ion exchangers are enhanced.

AMINOCHLORORUBBER

The nitrogenated rubbers which have been described up to the present time are only mediocre ion exchangers because of the weak polarity of the NH group introduced into the molecule. A more highly polar rubber can be obtained by treatment of chlorinated rubber with ammonia; in this way a part of the chlorine atoms is replaced by amine groups, and this confers a more basic character to the product.

To this end a 20 per cent solution of commercial tetrachlorinated rubber (approximately 64 per cent chlorine content), the same quantity of ammonia, and a small proportion of emulsifying agent (a sulfonated product) are heated in an autoclave for 3 hours at 150° C. After cooling, the brownish mass, which is insoluble in all ordinary solvents for rubber, is separated, dried, and washed with alkaline water.

The product thus obtained contains 4.1 per cent of nitrogen and 27 per cent of chlorine, and approximates the composition $(C_5H_7)_4(NH_2)Cl_3$ (calculated 3.7 per cent of nitrogen and 26.9 per cent of chlorine).

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences*, Vol. 230, No. 3, pages 298–299, January 16, 1950.

When pulverized, compressed under a load of 100 kg. per sq. cm. at 150° C, and granulated to a particle size of 0.5–1mm., it functions as an anion exchanger with relatively concentrated acids. Thus, the following quantities of hydrochloric acid at four different concentrations were retained:

Normality of HCl	Grams of HCl per kilogram of product
1 *N*	118.8
0.2 *N*	104.6
0.02 *N*	34.8
0.001 *N*	10.3

The product is washed with 2 per cent aqueous sodium carbonate to remove fixed hydrogen chloride, and then with water to the neutral point.

A new analysis of the regenerated product shows that its original composition remains practically unaltered during these manipulations. The product is stable, is remarkably inert toward all ordinary solvents, and has a high capacity as an anion exchanger. However, it can be used only to bind relatively concentrated acids, because its feeble basicity prevents its functioning as a good exchanger of anions in the purification of water, where the concentration of fixed acids liberated is very low.

REFERENCES

[1] Austerweil, *Bull. soc. chim.* 6, 63 (1939); French patents 832,866 and 842,115 (1938); *Rev. gén. caoutchouc* 21, 122 (1944): RUBBER CHEM. & TECHNOL. 20, 769 (1947).
[2] Austerweil, *Compt. rend.* 226, 799 (1948); *Bull. soc. chim.* [5] 15, 948 (1948).

IMPACT RESILIENCE AS A FUNCTION OF TEMPERATURE *

B. B. S. T. BOONSTRA

RUBBER FOUNDATION, DELFT, HOLLAND

INTRODUCTION

The influence of temperature on the resilience of rubberlike materials has been recognized for a long time; in fact, the lack of resilience of rubberlike materials at elevated and at subnormal temperatures is one of the reasons why efforts, which were finally successful, were made to develop a method for vulcanizing natural rubber. When not vulcanized, rubber tends to harden when cold and to soften when heated, whereas after vulcanization it retains its rubberlike properties through a range of temperature much greater than that of unvulcanized rubber.

The extreme limit of minimum resilience corresponds to the brittle point, for the determination of which various methods have been proposed[1]. The ultimate limit would be the temperature at which the rubber loses its strength. For most pure-gum vulcanizates of synthetic elastomers, this limit does not much exceed $-100°$ C, and it is considerably higher for pure-gum vulcanizates of natural rubber and for carbon black mixtures.

The most precise method of determining the brittle point is by means of a pendulum, which is made to strike the rubber sample from a certain height, h_0; the height h to which the pendulum rebounds is then measured. The resilience R, is defined by the expression:

$$R = \frac{E^1}{E_0} = \frac{h}{h_0},$$

whereby 100 R = the recovered energy in per cent.

Mullins[2] has described measurements of this resilience for various elastomers as a function of the temperature. He has also studied the influence of carbon black in GR-S and of plasticizing agents in Neoprene GN-A.

The present paper describes tests of vulcanizates, both pure gum and some containing carbon black, prepared from a series of fifteen different elastomers, some old, others of very recent origin. Natural rubber was included as a basis of comparison for evaluating the resilience of the various types of elastomers.

OPERATING TECHNIQUE

The measurements were made with a rebound resiliometer of the pendulum type of Lüpke[3]. The test-specimens, in the form of discs 40 mm. in diameter and 12.7 mm. thick, were set in an anvil which almost entirely enclosed them and left only a face of approximately 32 mm. exposed to the impact of an oscil-

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Revue Générale du Caoutchouc*, Vol. 27, No. 7, pages 409–414, July 1950. This paper is Communication No. 123 of the Rubber Foundation, and the investigation represents part of a comparative study of natural and synthetic rubbers undertaken by the Research Department of the Rubber Foundation. The author wishes to thank A. van Rossem for the interest which he has shown in this work.

lating rod. The anvil was mounted on a solid steel cylinder, 8 cm. thick, firmly attached to a brick surface. The whole assembly, carefully heat-insulated, was enclosed in a jacket equipped for the circulation of a cold or hot liquid. For measurements at all temperatures other than room temperature, the test-specimens were held for 15–20 minutes at the temperature of testing before making a measurement. They were then placed in the apparatus, where they were allowed to remain for five minutes more, with the opening covered by cotton. This was then removed, and the measurement was carried out immediately.

For some of the elastomers, the times of contact at the moment of impact also were measured. To do this, the surface of contact was coated with a thin film of a solution of conductive rubber in which was a flat helical spring in the form of a very fine silver wire. The latter was connected to one terminal of an electric condenser, the other terminal of which was connected, by means of a resistance, to the oscillating rod of the resiliometer. When the rod touched the silver wire, the condenser discharged; after impact, this discharge stopped, and the drop in potential made it possible to measure the time of contact. The principle of this method has already been described in an earlier publication[4].

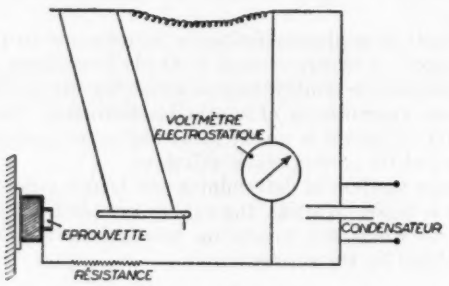


FIG. 1.—Schematic design of the apparatus for measuring the time of impact. (*Éprouvette* is the test-specimen.)

Figure 1 shows the arrangement of the electric circuit. The measurements of the times of contact were carried out during repeated impacts of the rod, which was allowed to oscillate freely and thus to rebound successively until its amplitude became too small to be measured with any reasonable degree of precision.

Table 1 shows the compositions and the times and temperatures of vulcanization of the various mixtures.

RESULTS AND DISCUSSION

Figure 2 shows the results of the resilience measurements of pure-gum vulcanizates. The resilience values are plotted against temperature, and the resulting curves all show more or less pronounced minima below room temperature. The temperature corresponding to the minimum value of the resilience depends on the type of elastomer, and is relatively high for elastomers which have high brittle points, *e.g.*, Hycar OR-15 (−20° C), Hycar OS-10 (−18° C), Perbunan-Extra (−29° C), and Perbunan-35 (−20° C), all of which contain relatively high proportions of styrene or acrylonitrile. When polymerized,

TABLE 1

COMPOSITION OF THE MIXTURES

	Natural rubber		GR-S		Neoprene GN-A		Neoprene F.R.		Butyl		Perbunan (German Extra)		Hycar OR-15		GR-S (41° F)		Buna-S (German)	
Polymer	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Zinc oxide	5	10	5	5	5	5	5	5	3	3	5	15	5	5	3	3	10	10
Antioxidant	1.5	1.5	1	1	2	2	2	2	—	—	1	2	—	—	1.2	1.2	1	1
Altax	—	—	—	—	—	—	—	—	—	—	—	—	1.25	1.25	—	—	—	—
Captax	0.8	0.8	—	—	—	—	—	—	0.5	0.5	—	—	—	—	—	—	—	—
Permalus	—	—	—	—	—	—	1	1	—	—	—	—	—	—	—	—	—	—
D.P.G.	0.5	0.5	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Vulkazit-AZ	—	—	—	—	—	—	—	—	—	—	1.8	1.8	—	—	—	—	1.8	1.8
Tuads	—	—	0.2	0.2	—	—	—	—	1	1	—	—	—	—	—	—	—	—
E.P.C. Black	—	44	—	50	—	30	—	30	—	50	—	57	—	50	—	50	—	52
Dibutylphthalate	—	—	—	—	—	—	—	—	—	—	—	—	—	20	—	—	—	—
Tricresylphosphate	—	—	—	—	—	—	—	—	—	—	—	30	—	—	—	—	—	17.5
Stearic acid	1	2	1.5	1.5	0.5	0.5	0.5	0.5	1	1	2	2	1.5	1.5	—	—	2	2
Extra plasticizer	—	10	—	8	—	—	—	—	—	—	—	10	—	—	—	4	—	10
Sulfur	1.75	2	2	2	—	—	—	—	2	2	1.5	1.5	1.25	1.5	2	2	1.5	1.5
Magnesia (extra light)	—	—	—	—	4	4	5	5	—	—	—	—	—	—	—	2	—	—
Santocure	—	—	—	—	—	—	—	—	—	—	—	—	—	—	1.65	1.65	—	—
Vulcanization (min.)	20	20	30	60	15	15	15	15	40	60	25	25*	30	45	40	40	20	20
Temperature ° C	142	142	142	142	152	152	152	152	152	152	142	142	152	152	142	142	142	142
° F	287	287	287	287	306	306	306	306	306	306	287	287	306	306	287	287	287	287

* The Perbunan was vulcanized 30 minutes.

TABLE 1 (*continued*)

	Perbunan-35 (American)		Perbunan-26 (American)		Perbunan-18 (American)		Thiokol F.A.		Hycar OS-10	
Polymer	100	100	100	100	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5	10	10	10	10
Antioxidant	1	1	—	—	—	—	—	—	1.5	1.5
Altax	1	1	1	1	1	1	0.3	0.3	—	—
Captax	—	—	—	—	—	—	—	—	—	—
D.P.G.	—	—	—	—	—	—	0.1	0.1	—	—
Santocure	—	—	—	—	—	—	—	—	1.2	1.2
Tuads	—	—	—	—	—	—	—	—	0.2	0.2
E.P.C. black	—	50	—	50	—	50	—	40	—	50
Dibutylphthalate	—	10	1	10	—	—	—	—	—	—
Tricesylphosphate	—	—	—	—	—	—	—	—	—	—
Extra plasticizer	—	—	—	—	—	—	—	—	—	8
Stearic acid	1	1	1	1	1	1	0.5	0.5	1	1.5
Sulfur	1.5	1.5	1.5	1.5	1.5	1.5	—	—	2	2
Vulcanization (min.)	40	40	40	40	60	120	20	20	20	25
Temperature ° C	142	142	142	142	142	142	147	147	142	142
° F	287	287	287	287	287	287	295	295	287	287

styrene and acrylonitrile yield products which are hard and brittle at room temperature, and which have very high brittle points. It would be expected, then, that the incorporation of 35–50 per cent of these monomers in a butadiene chain would result in a copolymer considerably stiffer and with a considerably higher brittle temperature than those of the corresponding pure polybutadiene. Thus German Perbunan (brittle point −37° C), Perbunan-26, and particularly Perbunan-18 (brittle point < −68° C) contain lower percentages of acrylonitrile than does Hycar OS-10 (brittle point −18° C). Also GR-S (brittle point −59° C) contains less styrene than does Hycar OS-10.

Consequently, as was to be expected, the resilience curves show minima proportionate to the higher brittle temperatures of Hycar OS-10 and GR-S. Likewise the curves show that the minimum resilience values of elastomers with high acrylonitrile contents, such as Perbunan-35, Perbunan-Extra, and Hycar OR-15, appear at higher temperatures than do the minimum values of types of elastomers containing lower acrylonitrile contents, *e.g.*, Perbunan-26. However, the temperatures found for Perbunan-26 are higher than those of Perbunan-18, with its lower acrylonitrile content.

The difference between the temperature of the brittle point and the temperature at which the resilience is a minimum depends on the particular elastomer. For example, these temperatures are practically the same; *i.e.*, approximately −40° C, for Thiokol-FA; whereas the majority of elastomers show minimum resilience temperatures which are definitely higher than their brittle points.

If, now, the resilience values of the various elastomers are compared, on the basis of temperature, as is shown in Figure 2, it will be found that natural rubber gives the highest values in the temperature range from −20° C to 100° C. Below −20° C, some elastomers show higher values than does natural rubber, but these are on the parts of the curves to the left of the minimum values. In the major part of the range in question, the products have become stiff and their resilience can no longer be considered as a rubberlike property.

It can safely be said, therefore, that natural rubber is more resilient than any synthetic elastomer examined within the temperature range where the products can be regarded as still possessing rubberlike properties.

To facilitate a comparison of the four diagrams in Figure 2, the curve of natural rubber is repeated in each diagram. Figure 2A shows an unusual peculiarity, *viz.*, the difference, at low temperatures, between vulcanized pure-gum rubber and unvulcanized rubber. The behavior of the latter, the maximum resilience of which lies below 0° C, is at variance with the generally accepted theory according to which vulcanization improves the resistance of rubber to cold. In this connection, it is well to consider the observations of Somerville[5], who pointed out that the progressive hardening of unvulcanized rubber at temperatures around −30° and −40° C is much slower than that of a pure-gum vulcanizate containing 2 per cent of sulfur under similar conditions.

Broadly speaking, the hardening of rubber and a corresponding loss of resilience at low temperatures are attributable to two causes. The first of these is the progressive stiffening of all rubberlike materials when cooled, which is caused by the progressively slower thermal movements of the chain segments. This hardening reaches a maximum when complete solidification takes place at the second-order transition point. Below this point, the elastomer resembles a transparent glass which can be fractured by impact. This solidification is characterized by the fact that it is reversible; in fact, when heated, the material recovers almost completely its rubberlike properties.

The second cause of hardening and loss of resilience, and a less general one,

is crystallization. Contrary to the first cause, there is a certain lag in this phenomenon. Wood[6] has made a thorough investigation of the rate and mechanism of this crystallization. To melt the crystals which have been formed at some definite temperature, it is necessary to heat the rubber well above this temperature.

In the resilience tests in the present work at temperatures below 0° C, the test-specimens were generally allowed to harden for about twenty minutes. Even at −25° C, where the rate of crystallization attains its maximum value, there was very little crystallization in the unvulcanized natural rubber during these first twenty minutes, as the experiments of Wood[6] also showed. Accordingly, any influence of crystallization in the samples of crude rubber may be regarded as negligible. In pure-gum vulcanizates, crystallization is even less advanced; in fact, the rate of crystallization is at least twenty to one-hundred times slower than in unvulcanized sheet.

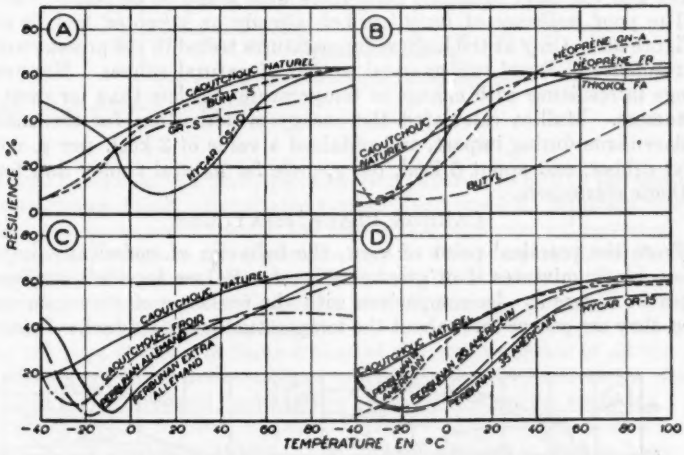


FIG. 2.—Impact resilience of pure-gum vulcanizates as a function of temperature.

It may, therefore, be safely assumed that in the resilience tests of both raw and vulcanized rubber, crystallization has no significant influence on the hardening and loss of resilience which occur at temperatures below 0° C.

It is evident from Figure 2A that crude sheet rubber which has been masticated for three minutes on a warm tight laboratory mill gives resilience values which are lower than those for the same rubber which has not been so masticated. In fact, the resilience at low temperatures of the masticated rubber is more nearly like that of the pure-gum vulcanizate.

This superiority of crude rubber over vulcanized rubber with respect to resistance to cold can be explained by assuming that the reaction with sulfur is the cause of the increased hardening on cooling. It is known, in fact, that resistance to cold depends on the accelerator in the rubber. However, it is difficult to attribute to this same mechanism the fact that the resilience of masticated rubber at low temperatures is lower than that of unmasticated rubber; and one is inclined rather to assume that a certain amount of crystalliza-

tion occurs. Actually, the mobility of the chain segments in masticated rubber is greater than that in the same rubber before mastication, as is evidenced by the viscosity and plasticity of the two products. In addition, the degree of crystallization is greater in the masticated rubber than in the same rubber which has not been masticated. This has been proved conclusively for highly masticated rubber.

Above room temperature, the resilience of masticated rubber decreases more than does that of unmasticated rubber, whereas the resilience after vulcanization continues to increase with rise in temperature. This is because of plastic flow in the masticated rubber and because of the very great decrease in this plastic flow as a result of vulcanization.

GR-S and German Buna-S showed lower values than those of natural rubber almost throughout the temperature range, and "cold rubber" had even less resilience at temperatures below room temperature. "Cold rubber" showed a minimum resilience around $-25°$ C, whereas the minimum values for natural rubber and the older synthetic elastomers were found to be below $-40°$ C.

The poor resilience of Butyl rubber, already an accepted fact, is evident in Figure 2B. Only at the highest temperatures tested in the present work was the resilience of Butyl rubber equal to that of natural rubber. However, the change in resilience with change in temperature was less than for most other elastomers. Mullins calculated the energy of activation for the molecular displacements during impact, and obtained a value of 3 kcal. per g.-mole for Butyl rubber, and about 6 kcal. per g.-mole for natural rubber and for most synthetic elastomers.

CARBON BLACK MIXTURES

From the practical point of view, the behavior of technically important carbon black mixtures if of greater interest. Values for their resilience are shown in Figure 3. In comparison with the resilience of pure-gum vulcanizates, they are poorer throughout the temperature range studied. Below 0° C,

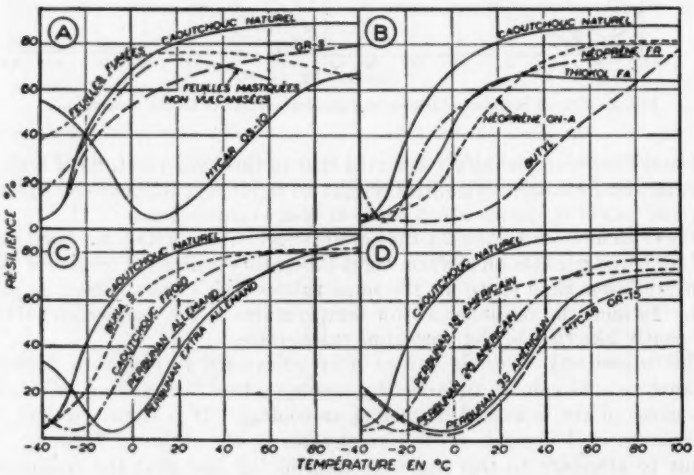


FIG. 3.—Impact resilience of carbon black vulcanizates as a function of temperature. (*Temps en millisecondes* is the time in milliseconds; *Rebondissement* is the rebound resilience; *Feuilles fumées* is smoked sheet rubber.)

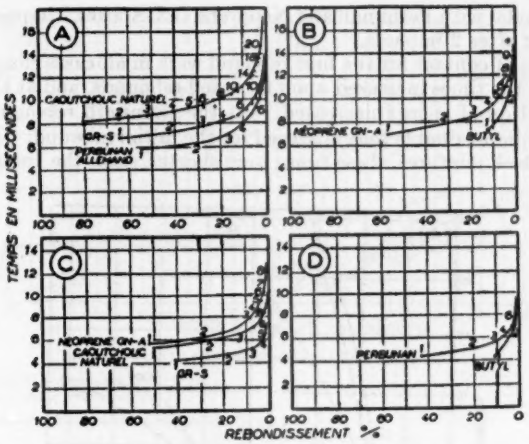


FIG. 4.—Time of contact for successive impacts.

(A) and (B) are pure-gum vulcanizates.
(C) and (D) are carbon black vulcanizates.

the natural rubber-carbon black vulcanizate is superior to any of the synthetic elastomer-carbon black vulcanizates except Neoprene-FR, although the difference is less pronounced than in the case of the pure-gum vulcanizates.

At room temperature and higher, natural rubber compares favorably with its competitive elastomers, Buna-S, GR-S, and "cold rubber"; it is, however, surpassed by various types of Neoprene, and, surprisingly enough, by Thiokol-FA within a short temperature range.

The old type of German Buna-S showed the best resilience of all the synthetic elastomers which are capable of replacing natural rubber at the present time, while the more recent "cold rubber" showed the poorest resilience. It is well, from this point of view, to examine Table 1 again, which gives the compositions of the various mixtures. The Buna-S mixture is seen to have contained 28 parts of plasticizer per 100 parts of polymer; the natural-rubber mixture 8 parts, and the "cold rubber" mixture 4 parts.

In all cases except the GR-S mixture, a high proportion of blown asphalt was used as the plasticizer, and this asphalt seems to have impaired the resilience at low temperatures. To Buna-S was added 18 parts of tricresylphosphate, and this plasticizer unquestionably improved the resilience below 0° C. This is the reason why technical mixtures do not give a true picture of the qualifications of the elastomers themselves in actual service.

As was to be expected, Butyl rubber showed the lowest resilience of any of the elastomers studied.

TIME OF CONTACT DURING IMPACT

Figure 4 gives the results of a series of measurements of the time of contact during impact as a function of the resilience for successive impacts.

It will be noted, first of all, that the pure-gum natural rubber mixture was capable of making the pendulum rebound 20 times, while still retaining 2 per cent of its initial energy. With GR-S, 2 per cent of the initial energy remained

after 10 impacts; with Perbunan and Neoprene GN-A after 7 impacts, and with Butyl rubber after 2 impacts.

The times of contact for the first rebound were in all cases close to 6–7 milliseconds; and the times increased upon repeated rebounds, and at the same time the consumption of energy decreased. At the twentieth rebound the time of contact was almost double that observed for the initial rebound. In the case of the carbon black mixtures, these times were shorter, since the vulcanizates were harder.

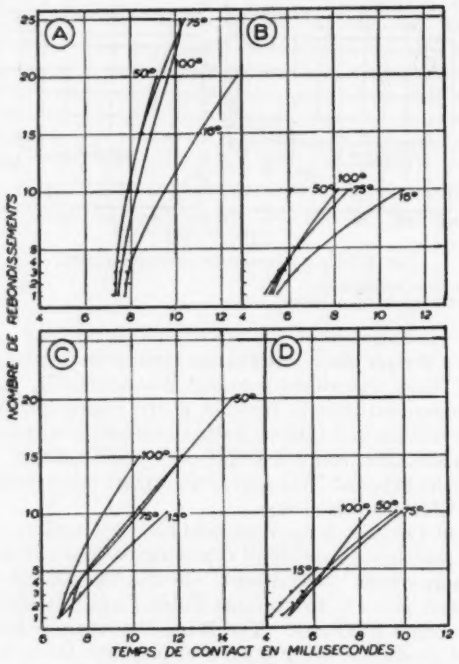


FIG. 5.—Time of contact at different temperatures.

(A) Pure-gum natural rubber vulcanizate.
(B) Natural rubber-carbon black vulcanizate.
(C) Pure-gum GR-S vulcanizate.
(D) GR-S-carbon black vulcanizate.

(*Nombre de rebondissements* is the number of rebounds; *Temps de contact en millisecondes* is the time of contact in milliseconds.)

The times of contact as measured in the present work were approximately one-half those recorded by Mullins. However, the latter operated with a complicated pendulum, equipped with a piezoelectric crystal, with which the times of contact were longer than with the Lüpke pendulum. More recent experiments by Mullins[7] have given results which agree with the times of contact indicated on Figure 4.

Times of contact were likewise measured at elevated temperatures, and are recorded for successive impacts on Figures 5, 6, and 7. In the case of pure-gum vulcanizates, the curves show displacements with temperature which are in accord with the trend of the resilience curves as a function of temperature. At

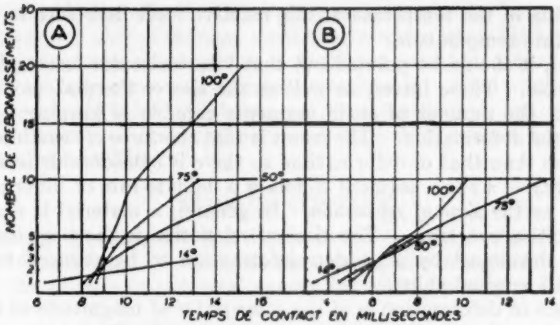


FIG. 6.—Time of contact at different temperatures.

(A) Pure-gum Butyl vulcanizate.
(B) Butyl-carbon black vulcanizate.

(The ordinate and abscissa are the same as in Figure 5).

the temperature where the resilience of a given vulcanizate attains its maximum value, the time of contact is the shortest, and the curve of the time of contact as a function of the number of impacts is the steepest. This was found to be not quite true of the vulcanizates containing carbon black. In the case of natural rubber, the optimum temperature seemed to be around 50° to 75° C; for GR-S, Butyl rubber, the Perbunans, and Neoprene GN, it was about 100° C or higher.

THEORETICAL CONSIDERATIONS

It is possible to explain in a qualitative way the minimum of the curve by assuming that the part of the curve located at the right of the minimum indicates a true rubberlike kinetic elasticity. In other words, the energy developed by the process of deformation, which finally makes the pendulum beam recoil, originates in the kinetic movements of the chain molecules. This energy is analogous to that which is manifest when a gas is compressed within a cylinder.

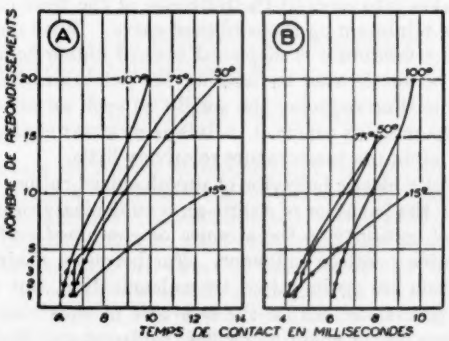


FIG. 7.—Time of contact at different temperatures.

(A) Pure-gum Neoprene GN-A vulcanizate.
(B) Neoprene GN-A carbon black vulcanizate.
(The ordinate and abscissa are the same as in Figures 5 and 6.)

With lowering of the temperature, this reactive force decreases in proportion to the absolute temperature.

However, it should be pointed out that intermolecular forces play a more important role. These forces, as well as the slower thermal movement, are able to limit the number of chain segments capable of keeping up with the rapidity of the deformation. The result is that the force of reaction during recovery is less than that of deformation, so there is considerable loss of energy. The capability of a chain segment to follow a definite rate of deformation may be denoted as the *time of relaxation*. In general, a material is characterized by its relaxation spectrum. The time of relaxation is the time necessary for the energy developed by a sudden deformation to be reduced to a certain fraction of its original value.

If the rate of deformation is of the same order of magnitude as the greater part of the time of relaxation, the stresses set up partially disappear during the deformation and, after retraction, a very small part of the energy is recovered.

At low temperatures, the times of relaxation increase, because the ratio of the forces of thermal movement to the intermolecular forces changes in favor of these latter. As a result, there is, during a given time of impact, a notable loss of energy by friction, and the resilience is, therefore, lower. At still lower temperatures, the intermolecular forces become completely predominant with respect to the thermal movement, which becomes very slow, and the material is then so stiff and hard that, on impact, the chain molecules no longer have time to give way. The interatomic distances are changed, and the forces resulting from this deformation furnish the major part of the energy of deformation. Under these conditions, the resilience has the character of a potential elasticity, and the mechanical losses again decrease. This rebound resilience can be compared to that of billiard balls. The deformation is smaller than in the case of kinetic elasticity, whereas the stress exerted is much greater. The percentage of the energy stored up temporarily is in all cases the same. The product: mean energy $\times$ deformation, corresponds, in the case of kinetic elasticity, to a small stress and high deformation and, for the potential elasticity of the frozen hard material, to a small deformation and a considerable force. Rubberlike elasticity may be said to be the kinetic elasticity, which is characterized by high deformation and low mean energy.

This theory takes into account the influence of the time of deformation on the position of the minimum on the resilience curve. With increase in the rate of deformation, the minimum is displaced toward higher temperatures. The deformation can be accelerated by making the pendulum fall from a greater height, at the same time reducing the weight to such an extent that the consumption of energy remains constant. Relatively great changes in the time of impact affect the minimum temperature relatively little.

The characteristic elastic behavior of unvulcanized rubber at low temperatures in relation to the behavior of a pure-gum vulcanizate cannot be attributed with any degree of certainty to the absence of combined sulfur, which must, nevertheless, exercise a certain influence. Furthermore, chains which are ruptured by mastication are again united by vulcanization, but this union takes place at random points and not on the last unit of each chain. As a result, in a substance composed of chain molecules, ruptured and then reunited, there are a large number of "loose ends" or terminal chains, which at low temperatures play an important part during the plastic deformation of vulcanized polymers[8].

Unquestionably the effects of time are likewise important here, not only the time of impact but also of storage, particularly when crystallization occurs.

According to some observations, a highly masticated rubber crystallizes more readily than the same rubber before mastication. This would explain the greater resilience of rubber which has not been masticated, but, on the other hand, would not explain its superiority over vulcanized rubber, which, without doubt, crystallizes still less.

TIME OF CONTACT

The velocity of the pendulum beam at the moment when it strikes the rubber can be calculated on the basis that the kinetic energy of the pendulum is equal to the change in potential energy brought about by a fall of 10 cm. height.

$$0.5\ mv^2 = mgh$$
$$v^2 = 2\ gh = 19.620$$
$$v = 140 \text{ cm. per sec.}$$

where g is the gravity constant of 981 cm. per sec.^{2}, and h is the fall of 10 cm.

The pendulum has a length of 200 cm.; hence, its time of oscillation T, is:

$$T = \pi \sqrt{\frac{200}{981}} = 3.14C\ \sqrt{0.21} = 1.44 \text{ second}$$

and the time of fall of the rod is 0.72 second.

If the deformation is assumed to be a sinusoidal function of time, the velocity of the pendulum then decreases cosinusoidally with time, *i.e.*, this rate:

$$\frac{dx}{dt} = \frac{2\alpha\pi}{T} \cos \frac{2\pi t}{T}$$

is a maximum for $t = 0$, where T is the time of oscillation, t is the time, and α is the amplitude.

Here T is twice the time of contact T_c, so α can be calculated from the expression:

$$\alpha = \frac{140T_c}{1.000 \times 3.14}.$$

In the case of a pure-gum natural-rubber mixture, the time of contact of which is 8 milliseconds, the amplitude α is:

$$\frac{140 \times 8}{1.000 \times 3.14} = 0.36 \text{ cm.}$$

Mullins reports a maximum deformation of 0.3 cm. for a GR-S mixture loaded with carbon black, whereas in the present work the same mixture showed a time of contact of about 4 milliseconds and a deformation of 0.18 cm.

With a view to determining to what extent dynamic deformation and static deformation differ, samples of rubber of the Lüpke type were tested for deformation under increasing loads, with an oscillating rod similar to that of the Lüpke apparatus. The load was increased until it was the same as the energy of impact, *i.e.*, 3500 g-cm. The load was then reduced, and the energy consumed was again calculated. From the values of the energy consumed and the energy supplied, the static resilience can be calculated: static resilience = energy recovered/energy supplied.

TABLE 2

RESILIENCE AND STATIC AND DYNAMIC DEFORMATION OF VARIOUS PURE-GUM VULCANIZATES AT ROOM TEMPERATURE

Polymer	Lüpke resilience (%)	Time of contact (millisec.)	Deformation calculated by the time of contact (mm.)	Static deformation (mm.)	Energy of static deformation (kg.)	Static resilience (%)
Natural rubber	75 to 84	8.0	3.6	4.28	21.6	96
Neoprene GN-A	63	6.8	3.0	4.10	22.0	84
Butyl rubber	13	7.2	3.2	5.15	17.6	91
Perbunan	46	5.8	2.6	3.68	24.4	87
GR-S containing carbon black	32	4.2	1.9	3.60	25.1	83
Hycar OR-15	17	4.5	2.0	3.60	25.0	81
Neoprene-FR	63	7.3	3.3	4.28	20.5	88

The calculated values and the values measured experimentally for deformation and static resilience are given in Table 2.

Table 2 shows that the dynamic deformation values, calculated on the assumption that the process is a harmonic oscillation, are considerably lower than those of static deformation, even in the case of a pure-gum natural-rubber vulcanizate.

The static resilience is also considerably higher than the corresponding Lüpke value. The former indicates that static compression is an almost completely reversible phenomenon. As far as dynamic compression is concerned, a considerable proportion of the deformation during impact is irreversible.

This phenomenon is especially pronounced in the case of Butyl rubber, and to explain it, recourse must be had to the theory of the relaxation spectrum of plasto-elastic deformations[9]. It would appear that when the rate of deformation of Butyl rubber is approximately 100 cm. per second, most of the times of relaxation of the plastic deformations are in resonance, whereas this is not true of natural rubber, Neoprene, or GR-S. With nitrile rubbers, the proportion of acrylonitrile is of fundamental importance. Perbunan, containing approximately 25 per cent of acrylonitrile, shows a dynamic resilience of 46; Hycar OR-15, containing approximately 40 per cent of acrylonitrile, a value of only 17. The static resilience values of these two nitrile rubbers are 91 and 81, respectively. The effect of an increase in the proportion of acrylonitrile is to displace the peak of the distribution curve of the relaxation times toward the value of the time during which the impact deformation lasts. This is because the strongly polar CN groups have a notable stiffening effect.

REFERENCES

[1] Graves and Davies, *India Rubber World* **41**, 109 (1943); Liska, *Ind. Eng. Chem.* **36**, 40 (1944); Selker, Winspear, and Kemp, *Ind. Eng. Chem.* **36**, 157 (1944); Borders and Juve, *Ind. Eng. Chem.* **38**, 1066 (1946).

[2] Mullins, *Trans. Inst. Rubber Ind.* **22**, 235 (1946–7); RUBBER CHEM. & TECHNOL. **20**, 998 (1947).

[3] Lüpke, *Vanderbilt News* **3**, No. 6, 10 (1933).

[4] Wildschut, "Physical and Technological Investigations in Natural and Synthetic Rubbers," Elsevier Publishing Co., New York-Amsterdam, **1946**, p. 125; Boonstra, *Proc. 2nd Rubber Technol. Conf., London*, **1948**, p. 190.

[5] Somerville, *Proc. Rubber. Technol. Conf., London*, **1938**, p. 773.

[6] Wood, in "Advances of Colloid Science," Interscience Publishers, New York, **1946**, Vol. 2, p. 58.

[7] Mullins, private communication.

[8] Flory, *Ind. Eng. Chem.* **38**, 417 (1946).

[9] Simha, *Rheological Bull.* **13**, No. 4, 11 (1942); Tuckett, *Trans. Faraday Soc.* **42**, 83 (1946); Kirkwood, *J. Chem. Physics* **14**, 31 (1946); Kuhn, Kunzle, and Preismann, *Helv. Chim. Acta* **30**, 307 (1947).

ORGANIC SULFIDES AS VULCANIZING AGENTS OF RUBBER *

R. L. SIBLEY

MONSANTO CHEMICAL CO., NITRO, WEST VIRGINIA

Following Ostromislensky's work in 1915, several investigators have reported results in vulcanizing natural rubber without the use of sulfur. Sturgis and Baum[1], Vila[2], and Wolf, Deger, Cramer, and DeHilster[3] later extended this study to GR-S rubber. The vulcanization of GR-S rubber with a wide variety of several different families of organic sulfur compounds was described by Throdahl and Beaver.[4]

This last mentioned study reported only a portion of the work completed in the research and rubber testing laboratories of Monsanto Chemical Company, and this will now be extended to include other phases of the investigation completed prior to, concurrent with, and subsequent to, that described by Throdahl and Beaver. Following the adoption of mercaptobenzothiazole and derivatives thereof, employed either alone or activated by basic accelerators, the control of prevulcanization or scorchiness of rubber compounds has been a most serious problem. While this problem was in large part a physical or engineering problem, it also offered possibilities of improvement or of solution by chemical means. As one reasonable method of approaching this investigation, it was theorized that if sulfur in organic combination was stable at temperatures slightly above those experienced in rubber milling and processing operations, but was unstable and decomposed with liberation of sulfur only at temperatures met in the vulcanization step, satisfactory curing of rubber could be accomplished as desired, while the probability of scorching of the stock would be greatly reduced and possibly avoided. With this thought in mind, attention was given to various organic sulfides as possible so-called sulfur liberators. Several such compounds were tested in the following rubber stock selected for screening purposes:

Pale crepe rubber	100.0 parts
Zinc oxide	8.0 parts
Whiting	50.0 parts
Stearic acid	0.5 parts
Dibenzothiazyl dimethylthiolurea	2.0 parts
Diphenylguanidine	0.4 parts
Sulfur compound	As shown

Cure 3, 6, 9, 12, and 18 minutes at 298° F. Viscosity tests at 200° F.

The results obtained in one series of tests are shown in Table 1.

It is of interest to note that, whereas diethyl trisulfide is very stable, diethoxy disulfide is unstable and produces a very satisfactory cure with excellent

* An original contribution. This paper was presented before the Northern California Group, September 28, 1950.

nonscorching properties. However, this last product was not studied further because it was obtained in very poor yield, and had the highly objectionable property of being a strong lachrymator.

A second series of products is shown in Table 2, in which the same test formula was employed as in the previous test.

TABLE 1

Sulfur compound	Percentage used		Cure tests @ 298° F 3 min.	6 min.	9 min.	12 min.	18 min.	Plasticity @ 200° F 3 hrs.	5 hrs.	6 hrs.
		300%	1015	1065	1030	1010	—			
Sulfur	1.0	500%	2760	2935	2930	2840	—	674		
		Break	3135	3240	3250	2995	—			
		Elong.	735	725	725	715	—			
$(C_7H_5)_2S_2$	3.5			No cure						
$(C_7H_5O)_2S_2$	4.33			Not			532			
				tested			1898			358
							3510			
							640			
$(C_6H_5O)_2S_2$	3.0			No cure						
	6.0			No cure						
	8.0				89					
					218			353	407	
					370					
					670					
$(C_6H_5[NH_2]_2)_2S_2$	5.0			No cure						
$(CH_3 \cdot C_6H_3[NH_2]_2)_2S_2$	5.0			No cure						

All three of the tetrasulfides did produce some cure, but with varying degrees of scorchiness. By determining the plasticity of the stocks in the Williams plastometer, with preheating at 200° F, the control sulfur stock showed a flow number of 674 mm. after 3 hours. In tendency to cause scorching, dibenzoyl tetrasulfide was practically the same as sulfur itself, whereas diphenyl tetrasulfide and dibenzyl tetrasulfide gave flow results of 426 and 380 mm., respectively, after six hours' heating.

TABLE 2

Sulfur compound	Percentage used		Cure tests 3 min.	6 min.	9 min.	12 min.	Plasticity 3 hrs.	5 hrs.	6 hrs.
		300%	1015	1065	1030	1010			
Sulfur	1.0	500%	2760	2935	2930	2840	674		
		Break	3135	3240	3250	2995			
		Elong.	735	725	725	715			
$(C_6H_5)_2S_2$	2.0			No cure					
$(C_6H_5S)_2S_2$	4.6		No	205	248	265			
			cure	490	605	675		310	426
				515	985	965			
				715	825	800			
$(C_6H_5CO)_2S_4$	2.7		No	375	390	425			
			cure	970	1045	1150	572		
				1360	1570	1625			
				795	805	790			
	5.3		485	580	668	710			
			1370	1730	1885	2110	684		
			1945	2400	2365	2520			
			795	780	750	740			
$(C_6H_5CH_2)_2S_4$	5.0			18 min. cure		134			
						322			380
						829			
						700			

Of the many sulfur-containing organic compounds tested, several of the sulfides were compared in an experimental stock typical of a wire compound. Such a stock employed was the following:

Smoked sheet rubber	100.0
Whiting	148.5
Zinc oxide	64.5
Ozokerite	2.5
Stearic acid	0.6
P-33 black	0.8
Phenyl-beta-naphthylamine	2.4
Piperidinium pentamethylenedithiocarbamate	2.0

Cures were 45, 60, and 75 minutes at 266° F. Scorchiness was determined with the Williams plastometer, with preheating at 200° F, and the stocks were aged in an air bomb under a pressure of 80 pounds of air per sq. in. at 250° F, and under a load giving 50 per cent elongation. Only the 60-minute cure was aged. The results are shown below. In these tests, as in those previously shown, the quantity taken of the sulfur-containing material was sufficient to provide an amount of sulfur equivalent to that of the control stock, assuming that all of the sulfur present was liberated.

All of the organic sulfur compounds in Table 3 showed much less tendency to cause scorching than did sulfur itself. Moreover, all the compounds showed the desired instability when heated, and formed free sulfur within the rubber stocks. Whereas some of these sulfur-containing products apparently made available for vulcanization all of their sulfur content, others under the particular conditions apparently only did so to an intermediate extent. In gen-

TABLE 3

Sulfur compound	Percentage used		Cure tests 45 min.	Cure tests 60 min.	Cure tests 90 min.	Plasticity 15 min.	Plasticity 1 hr.	Plasticity 2 hrs.	Aged results 15 hrs.	Aged results 20 hrs.
$(C_3H_7)_2S_4$	3.36	200%	280	280	305				450	400
		400%	740	745	760	—	392	549	880	765
		Break	1270	1330	1300				1020	910
		Elong.	540	560	540				475	475
$(CSNH_3)_2S_2$	2.0		395	385	390				435	410
			980	965	945	—	662	700	880	—
			1430	1400	1300				880	700
			500	510	490				400	385
$(C_6H_5S)_2S_2$			325	340	350				330	185
			935	910	945	272	378	812	815	455
			1400	1475	1450				1040	545
			540	545	545				470	460
$\left(\begin{matrix}CH_3\\ \\ C_5H_{11}\end{matrix}\!\!>\!N-\right)_2S_2$	4.5		505	530	480					415
			1370	1425	1370	—	181	200	—	—
			1760	1425	1580					415
			480	400	430					200
Sulfur	0.6		565	660	625				630	510
			1640	1630	1645	712	922	—	—	—
			2075	1630	1800				1310	1025
$(C_3H_6O\cdot CS)_2S_2$	3.8		500	400	450				370	340
			605	590	645				505	305
			1435	1410	—	321	492	—	—	—
			1720	1630	1380				865	450
			485	450	385				360	370
$\left(\begin{matrix}CH_3\\ \\ C_5H_{11}\end{matrix}\!\!>\!N-C-S\right)_2S_2$	5.3		450	465	465					425
			1300	1250	1265	—	261	567	—	—
			1770	1690	1815					675
			500	505	515					370
$\left(\begin{matrix}C_2H_5\\ \\ C_2H_5\end{matrix}\!\!>\!N\right)_2S_2$	5.0	200%	410	420	415					
		400%	980	970	955	4 hr. test		690	Not run	
		Break	1460	1580	1415					
		Elong.	510	530	510					
$[O(CH_2)_4N]_2S_7$	3.7		505	515	495				470	425
			1290	1310	1280	5 hrs.	365		—	—
			1765	1790	1660	8 hrs.	600		560	475
			490	490	470				310	310

eral, the moduli of elasticity were from 10 to 15 per cent less than the control stock containing added sulfur, while the elongations were usually approximately the same or slightly higher in value. These stocks all aged less satisfactorily than did the control stock. Again, generalizations are difficult, but evidently the sulfurized amines are somewhat more unstable than the sulfurized hydrocarbons, although in the case of the last named class of compounds, the tetrasulfides, appear less stable to heat than do the disulfides. However, an insufficient number of tests are recorded to accept this statement as infallible. This is well illustrated by the group of sulfurized dioxybenzenes. In this group, catechol sulfide is inactive, whereas resorcinol and hydroquinone sulfides liberate sulfur under curing conditions.

The various organic sulfides tested were prepared by commonly recognized methods. Thus, diethoxy disulfide, diphenoxy disulfide and dibenzoyl tetrasulfide were obtained by adding sulfur monochloride, preferably in an inert solvent, to a suspension of an alcohol, a phenol, and a thiol acid, respectively, in an inert solvent. The diphenyl, dibenzyl and dipropyl tetrasulfides were obtained by reacting sulfur monochloride with a solution of the proper thiol in an inert solvent. The monoamine disulfides were obtained by reacting sulfur monochloride with the required secondary amine in an inert solvent. The two aromatic diamine polysulfides were obtained by reacting the amine and sulfur in alcoholic solution[5]. Diethyl trisulfide resulted from the reaction of diethyl sulfate with a cooled alcoholic solution of sodium trisulfide. Thiuram disulfide and ethylxanthic disulfide were obtained by oxidation of ammonium dithiocarbamate and sodium ethylxanthate, respectively.

In view of the excellent curing action of morpholine disulfide and especially of the outstanding nonscorching property of this compound, it was decided to select this particular compound for more complete and detailed investigation. Three different sulfides of morpholine were first investigated. The monosulfide contained only 15.7 per cent sulfur, in contrast to the 27.1 per cent sulfur content of the disulfide. Both were solid materials which melted at approximately the same temperature, viz., 124–126° C. Although the tetrasulfide contained 42.6 per cent sulfur, it was an oily, pastelike material with undesirable physical properties. The sulfur-liberating properties of the mono-, di-, and tetrasulfides of morpholine were tested in the following manner.

An experimental tread stock was mixed in the following proportions of ingredients: Smoked sheet rubber 100, carbon black 50, zinc oxide 5, stearic acid 3, pine tar 2, *p*-aminobiphenyl-acetone antioxidant 1, and *N*-cyclohexyl-2-benzothiazole sulfenamide 0.8. Other ingredients are set forth in the table. The cures were for 15, 30, 45 and 60 minutes at 275° F. Plasticity tests were carried out on the Mooney plastometer at 135° C. Aging tests were made in the air bomb for a 9-hour period at 121° C. The results are set forth in Figures 1 and 2.

The quantity of morpholine sulfide in all three stocks theoretically is that required to produce 1 per cent of sulfur on breakdown. The rate of breakdown of these sulfides, however, seems to vary, as is shown by the shortest curing period. All three sulfides yield cures equal to those obtained with sulfur itself, and all three of the organic sulfide stocks show a higher percentage retention of tensile strength after aging than does the sulfur containing stock.

The results of the plastometer tests showed that the morpholine tetrasulfide is slightly more scorchy than the sulfur stock, whereas the disulfide and monosulfide stocks are both much less scorchy than the sulfur control. Because of the physical nature and very satisfactory activity of the disulfide, it was selected

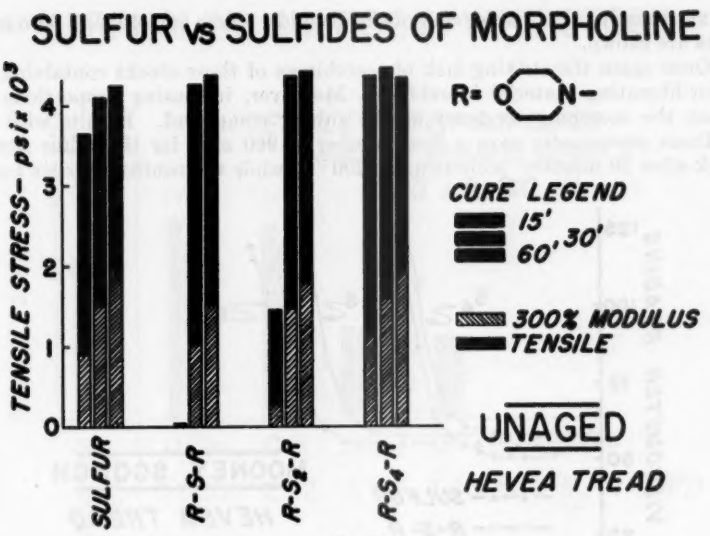


FIG. 1.

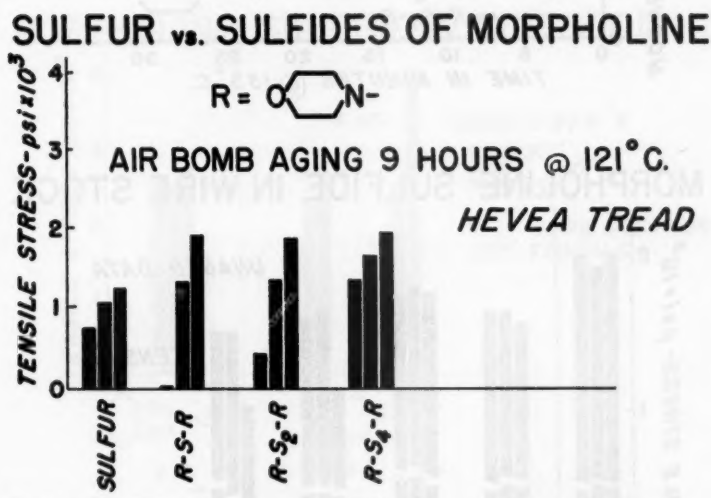


FIG. 2.

among the other sulfides of morpholine as most desirable for more extensive study.

One test was planned to determine the effect of varying quantities of morpholine disulfide in place of sulfur in a wire stock. With the exception of a change in the antioxidant to 2.4 parts of acetone-aniline, the same rubber compound was used as in the earlier test. Each group of three bars in Figures 4 and 5 show the results of 30, 45, and 60 minute cures at 266° F, except in the case of

the aged results with 7.4 per cent of the disulfide, where only 45- and 60-minute cures are shown.

Once again the striking lack of scorchiness of those stocks containing the sulfur-liberating material is evident. Moreover, increasing proportions decrease the scorching tendency of the rubber compound. Results with the Williams plastometer gave a flow number of 960 mm. for the sulfur control stock after 30 minutes' preheating at 200° F, while the results after six hours'

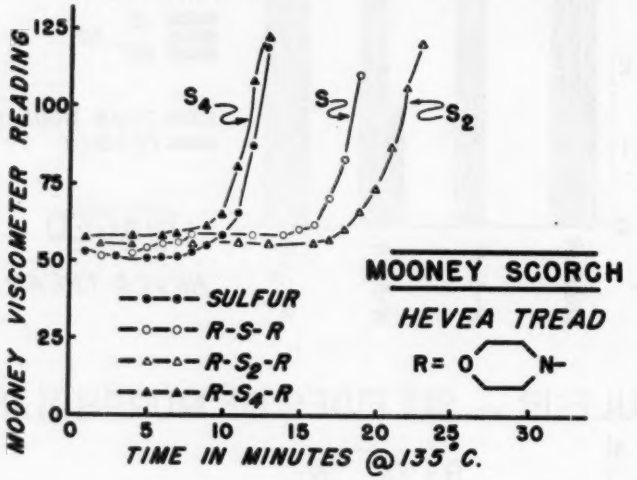


FIG. 3.

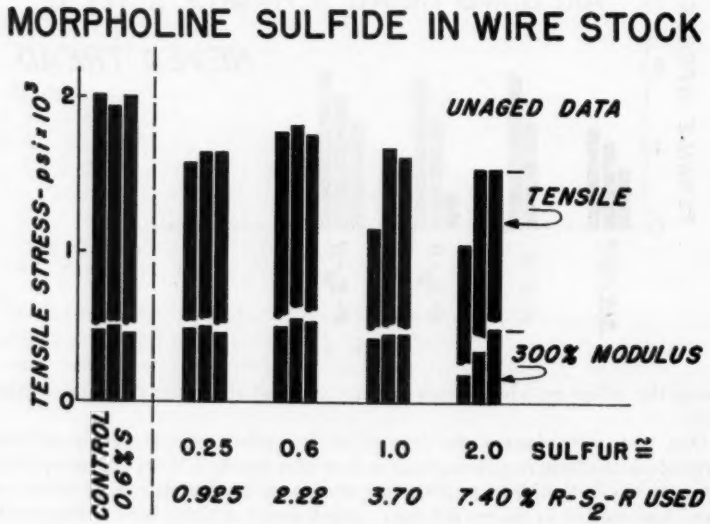


FIG. 4.

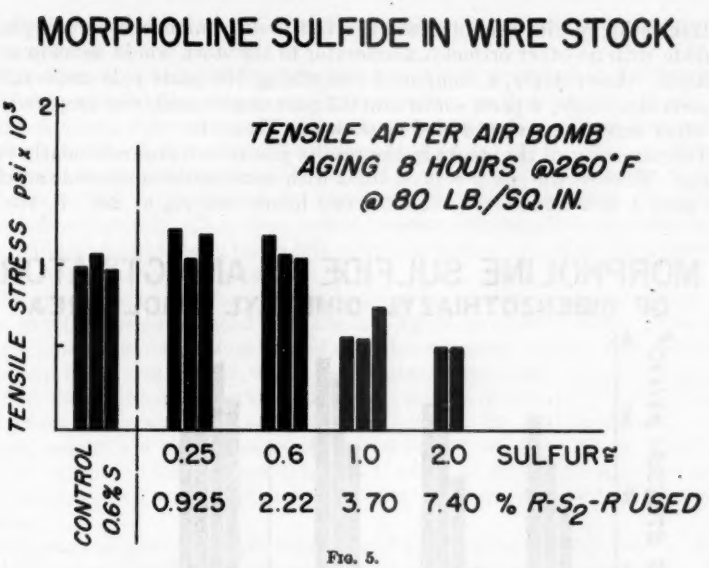


FIG. 5.

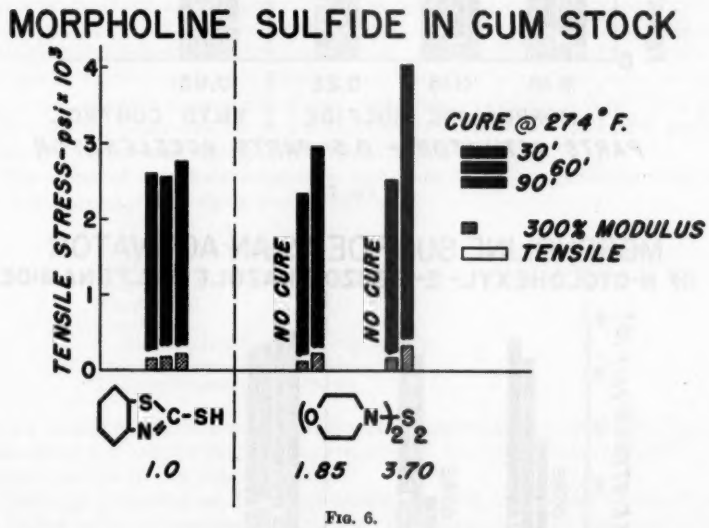


FIG. 6.

heating of the four morpholine disulfide stocks ranged from 459 to 600 mm. The persistence in cure of the sulfur liberator is particularly noticeable, while the use of less, or of a quantity up to nearly twice the weight equivalence of sulfur, does not materially affect either the unaged or the aged results. Higher proportions of the sulfur liberator are, as to be expected. a distinct disadvantage, particularly as regards aging results.

Interesting results were obtained in a test to determine whether morpholine disulfide with no other orthodox accelerator in the stock would develop a cure by itself. Accordingly, a compound comprising 100 parts pale crepe rubber, 10 parts zinc oxide, 3 parts sulfur and 0.5 part stearic acid, was prepared, and the other ingredients were added as shown in Figure 6.

The plasticity of the stocks in the results just shown are particularly interesting. Whereas the sulfur control stock with mercaptobenzothiazole acceleration gave a flow number of 412 after two hours' heating at 200° F, the two

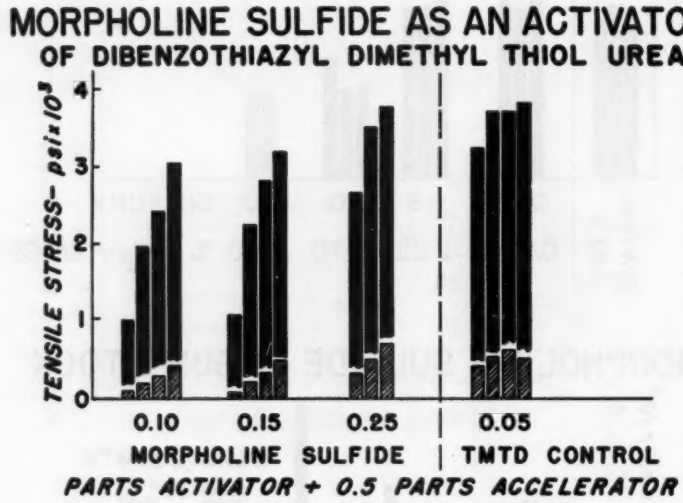


FIG. 7.

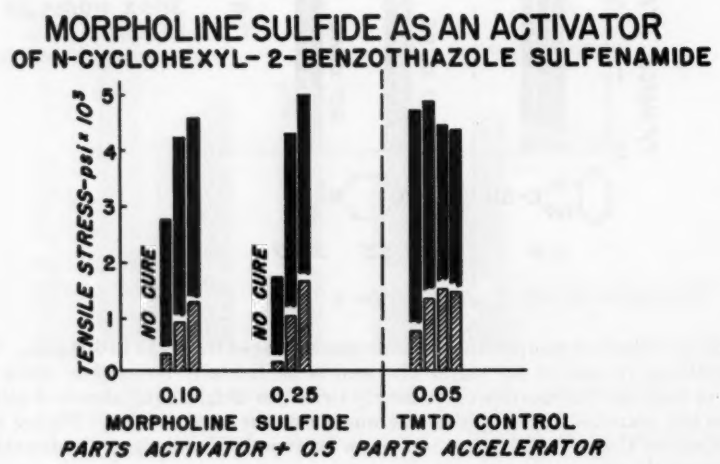


FIG. 8.

morpholine disulfide stocks yielded flow numbers of 221 and 211 mm. respectively, after 24 hours' heating.

To other stocks duplicating the base compound described in the preceding table were added increasing percentages of sulfur, so that the final stocks contained 4, 5, and 6 per cent total sulfur, but no accelerator. In all instances no cure was produced, even after 90 minutes' heating at 274° F. Hence, the cures effected in Figure 6 were due to the combined action of the morpholine disulfide and not to the sulfur liberated. Consequently the breakdown products of morpholine disulfide, other than sulfur, possess vulcanization accelerating action, and this fact has been taken into consideration by adjusting the accelerator ratio in work carried out later.

Morpholine disulfide, in addition to providing sulfur for vulcanization, also acts, as might be anticipated from the last figure, as an activator of mercaptobenzothiazole and derivatives thereof when used in small proportions. This fact is evident in Figures 7 and 8, which show tests of a stock comprising 100 parts of smoked-sheet rubber, 10 parts of zinc oxide, 3 parts of sulfur, 0.5 part of stearic acid, with accelerator and activator as shown in the test results. In these figures, results are shown for stocks cured for 30, 45, 60, and 90 minutes at 258° C, except for one instance (Figure 7), where no 90-minute cure was made, and the first two stocks (Figure 8), where no cure resulted in 30 minutes' heating.

Although somewhat higher quantities of morpholine disulfide than of tetramethylthiuram disulfide are required for activating mercaptobenzothiazole type of acceleration, the added safety factor in processing operations, as shown by the greatly increased resistance to scorching, makes the morpholine compound of considerable interest in this application. In the preceding two tables, the two stocks employing tetramethylthiuram disulfide activation were set up in four hours, whereas none of the stocks containing morpholine disulfide in place of the thiuram compound showed scorching tendencies after 12 hours' preheating at 200° F, as determined in the Williams plastometer.

The effect of morpholine disulfide in a P-33 black compounded stock was also determined. The stock was as follows:

Smoked sheet rubber	100
P-33 black	40
Zinc oxide	5
Stearic acid	1
Paraffin	0.75
p-Aminobiphenyl-acetone condensate	2
Dibenzothiazyl dimethylthiolurea	1.05
Diphenylguanidine phthalate	0.45

To this base stock there were added the other ingredients as shown in Figure 9, which gives the unaged results for cures of 6, 9, and 12 minutes at 284° F, and the aged results of the 9-minute cures.

Although improved modulus and tensile strength results were obtained with the higher ratio of morpholine disulfide, the stock still was not equal to the sulfur-containing control in properties. This is not surprising, since in this stock the total amount of sulfur present cannot exceed 0.31 per cent. Once again the greatly extended delay in scorching tendency is demonstrated. The sulfur control stock was set up after four hours' heating, whereas the sulfur-morpholine disulfide combination and the other two stocks showed no scorching after six hours. The most interesting results shown in this last table, however, are the outstanding properties of the stock containing a small addition of sulfur

with the vulcanizing adjunct. When compared with the sulfur control stock, the addition of a little sulfur to morpholine disulfide was found to delay scorching, develop higher moduli, and tensile strength, with about the same elongations, and also to produce a stock with better aging characteristics.

To explore this further, another stock corresponding exactly to that employed in the previous example was mixed, except that 40 parts of whiting were substituted for 40 parts of P-33 black. The cures were 3, 6, 9 and 12 minutes at 284° F, and the aged results for the 9-minute cure after aging in the air bomb for 18 hours under 80 pounds air pressure per square inch are shown in Figure 10.

These results prove convincingly that combinations of low sulfur with morpholine disulfide develop properties superior to those obtained with a normal sulfur ratio. The rate of curing can readily be adjusted to produce the desired effect of better unaged and aged moduli and tensile strength values, with

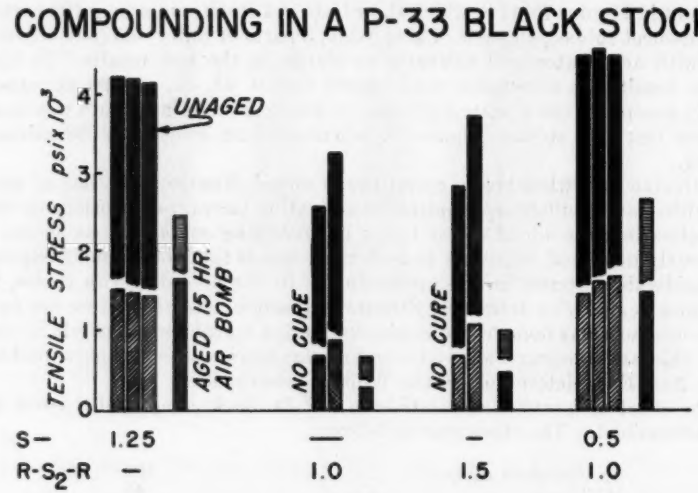


FIG. 9.

greatly lessened tendency to scorch. In this stock the sulfur control was set up after only 5 hours' preheating, while the three morpholine disulfide-sulfur combinations showed no scorching after 14 hours at 200° F. Apparently the most desirable results are obtained by the use of a total of approximately one-third the normal amount of sulfur supplied by the use of some free sulfur with the sulfur liberator, together with an adjustment in the amount of accelerator required.

Tests were carried out with the same stock previously described as a wire compound and which carried a heavy load of pigments, but in which the accelerator previously employed, *i.e.*, piperidinium pentamethylenedithiocarbamate, was replaced by a number of different classes of common accelerators. Naturally all the stocks that showed any vulcanization were slower in rate of curing than the earlier control stock which contained the dithiocarbamate type acceleration. A diphenylguanidine-morpholine disulfide stock showed no cure after 90 minutes at 275° F. Mercaptobenzothiazole, its disulfide, and two well known derivatives of mercaptobenzothiazole, all used in conjunction with

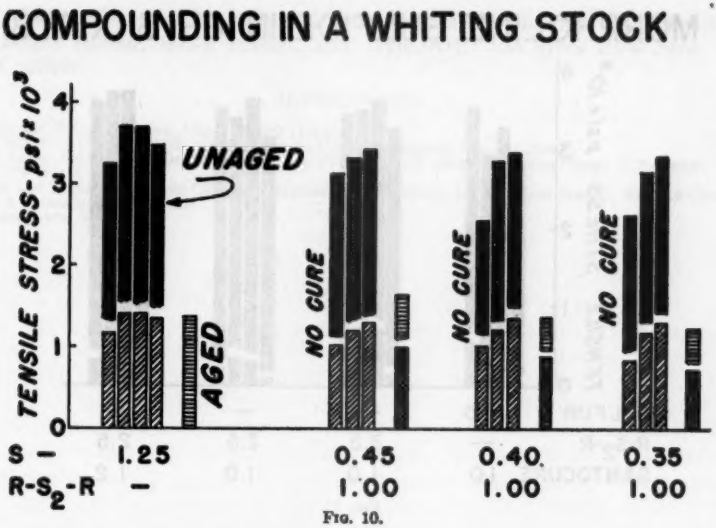


FIG. 10.

morpholine disulfide, produced cures in 90 minutes equal to the control containing sulfur, but none of these produced a stock that could be tested at shorter vulcanization periods. Butylaldehyde-aniline (1 per cent) with morpholine disulfide (3.5 per cent) yielded a vulcanizate in a low state of cure after 30 minutes at 275° F, but after 60 minutes this vulcanizate was equal in physical properties to the sulfur-containing control stock. Of the stocks that showed any cure, all showed less scorching than the control when tested in the Mooney plastometer.

Morpholine disulfide (3.5 per cent on the rubber) did not produce any cure in a Butyl rubber (GR-1) stock containing 0.5 part mercaptobenzothiazole acceleration after 20 minutes at 320° F. By adding 1 per cent of tetramethylthiuram disulfide, the results were greatly improved, although the rate of curing was slow.

In a Hycar-OR stock containing 60 parts of SRF Black, 5 parts of zinc oxide, 30 parts of dioctyl phthalate, and 1.0 part of stearic acid per 100 parts of Hycar, no cure was obtained in 10 minutes at 291° F with 1.5 parts of mercaptobenzothiazole disulfide and 3.5 parts of morpholine disulfide. In the 30-minute and 45-minute cures, higher tensile strengths and greater elongations but lower moduli of elasticity were produced than in the stock in which 2 parts of sulfur and 1.5 parts of mercaptobenzothiazole disulfide were added to the control.

Morpholine disulfide was also tested in a GR-S stock compounded as follows:

GR-S(X-478)	100
EPC Black (Kosmobile-77)	40
Zinc oxide	4
Stearic acid	2
Paraflux softener	10

Other ingredients added were sulfur, accelerator, and morpholine disulfide, as shown. The test results are given in Figure 11, where each series of bars shows

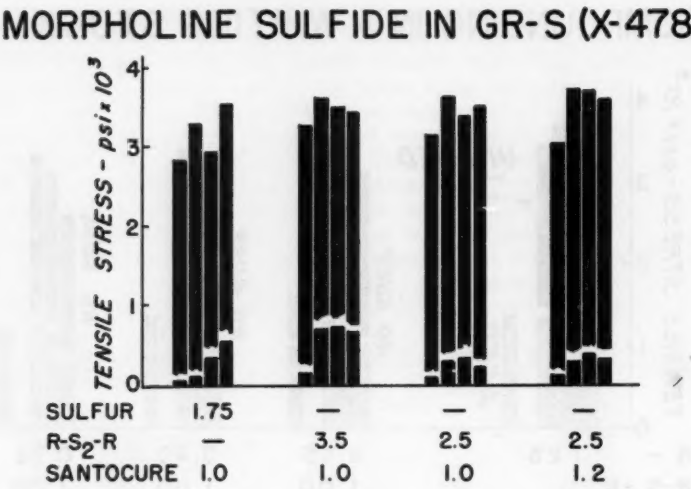


FIG. 11.

300 per cent moduli and tensile strength values obtained after cures of 30, 45, 60 and 90 minutes at 291° F.

Plasticity tests carried out in a Mooney plastometer showed no scorching for any of the stocks after 30 minutes' preheating. The results show clearly that a higher modulus, higher elongation stock by morpholine disulfide than by sulfur. Furthermore, scorching is satisfactorily controlled and hardness is normal. It is evident that variations are possible in the formula employed to develop the degree of cure as desired.

CONCLUSIONS

1. It has been demonstrated that a number of organic sulfides possess the property of breaking down under vulcanizing conditions in a rubber compound to produce a cure.

2. Although several scores of sulfur-containing organic compounds other than those discussed in this paper or described in other papers have been tested, as yet there appear possible no generalizations to serve as a guide to further exploratory studies.

3. Organic sulfur compounds which are unstable under temperature conditions higher than normal do not liberate all of their sulfur in all cases.

4. Organic sulfur compounds employed alone as vulcanizing agents usually produce slower-curing rubber stocks than does sulfur, and at the same time lessen greatly the tendency of the stock to scorch.

5. Stocks of satisfactory physical properties, superior aging characteristics, and outstanding freedom from scorchiness are obtained by the use of a fractional part of the normal sulfur requirement together with a sulfur liberator.

6. Morpholine disulfide is a good example of a sulfur liberator, and exhibits its greatest effects in conjunction with a mercaptobenzothiazole type accelerator.

7. Morpholine disulfide gives satisfactory cures when used in place of sulfur in natural rubber, GR-S rubber, and Hycar-OR, but gives slow cures in GR-I rubber.

REFERENCES

[1] Sturgis and Baum, *Ind. Eng. Chem.* **36**, 348 (1944).
[2] Vila, *Ind. Eng. Chem.* **34**, 1269 (1942); RUBBER CHEM. & TECHNOL. **16**, 184 (1943).
[3] Wolf, Deger, Cramer, and DeHilster, *Ind. Eng. Chem.* **38**, 1157 (1946); RUBBER CHEM. & TECHNOL. **20**, 775 (1947).
[4] Beaver and Throdahl, RUBBER CHEM. & TECHNOL. **17**, 896 (1944); Throdahl and Beaver, RUBBER CHEM. & TECHNOL. **18**, 110 (1945).
[5] German patent 86,096.

DETERMINATION OF FREE CARBON IN CURED RUBBER STOCKS *

I. M. KOLTHOFF AND R. G. GUTMACHER

UNIVERSITY OF MINNESOTA, MINNEAPOLIS, MINNESOTA

In the course of current studies on the interaction of rubber and carbon black, a method for the determination of the free carbon content of vulcanized rubber stocks, which is simple, rapid, and of an accuracy sufficient for control purposes, was developed.

The procedures which have been used for the control of rubber-carbon black batches may be classified in three groups. Widest adoption has been gained by the methods involving the degradation of the rubber matrix and most compounding ingredients by hot concentrated nitric acid. Typical of these is the current A.S.T.M. method[1]. Butyl rubber (GR-I) and Neoprene, which are resistant to nitric acid decomposition, cannot be analyzed in this way. McCready and Thompson[2] have suggested preliminary digestion of the sample in hot mineral seal oil to make the method applicable for Butyl rubber. The chief disadvantage of the nitric acid procedures is the difficulty experienced in filtration of the carbon, because the finely divided particles tend to run through the asbestos filter. Because some of the decomposition products of the rubber are retained by the carbon, the results are high and variable; an empirical correction of 0.95 must be applied. A recent modification by Louth[3] eliminates many of these disadvantages, but adds a few of its own. The procedure involves preliminary softening of the sample in boiling 1,1,2,2-tetrachloroethane (which makes possible analysis of Butyl rubbers and Neoprene), the use of ether to coagulate the carbon during the filtration, and drying of the carbon at 250° instead of 110° C to avoid application of the correction factor. The unpleasant nature of 1,1,2,2-tetrachloroethane and the possibility of violent reaction between the nitric acid and ether in the filtration step in spite of all precautions constitute the disadvantages of this procedure.

The extraction of the rubber by a high-boiling inert solvent has been little used, partly because of the length of time required[4].

The third group of methods involves dry distillation of rubber from the carbon black and inorganic fillers in an inert atmosphere and subsequent burning of the carbon black in oxygen. The method was first used for natural rubber by Decker[5] and modified for the analysis of GR-S by the National Bureau of Standards[6]. Bauminger and Poulton suggest collecting and weighing the carbon dioxide evolved in addition to the usual determination of the weight loss during the combustion[7]. These methods are rapid if two combustion furnaces are available. However, standard sample blanks must be run with each set of samples to correct a slight empirical error in the method. In addition, inorganic fillers which change weight during the two combustions may prove troublesome.

* Reprinted from *Analytical Chemistry*, Vol. 22, No. 8, pages 1002–1003, August 1950. This work was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the synthetic rubber program of the United States Government.

The method here proposed makes use of the fact that rubber containing ethylenic double bonds is oxidatively cleaved by *tert*-butyl hydroperoxide in the presence of osmium tetroxide. The resulting fragments are compounds of small molecular weight. The reaction has previously been used for the determination of polystyrene in GR-S[8]. The applicability of the method was tested by the analysis of natural rubber, GR-S, Butyl rubber, and Neoprene, and was found successful in each case.

OUTLINE OF METHOD

The sample is softened in gently boiling *p*-dichlorobenzene, and then treated with *tert*-butyl hydroperoxide in the presence of a catalytic quantity of osmium tetroxide. The mixture is filtered through a Gooch crucible. The carbon on the filter is washed with benzene, and then with dilute nitric acid and water to disolve inorganic fillers. The filter is dried at 350° C, cooled, and weighed. The carbon is burned off at low red heat, and the crucible is cooled and reweighed. The loss in weight represents the amount of carbon originally present.

REAGENTS

tert-Butyl hydroperoxide, commercial grade (minimum 60% *tert*-butyl hydroperoxide), is obtained from the Lucidol Division, Novadel-Agene Corporation, Buffalo, N. Y. The reagent is stable for several months if kept in a cool place.

Osmium tetroxide is prepared by dissolving 0.08 gram in 100 cc. of reagent grade benzene. The solution should be protected from light and discarded at the first appearance of a black precipitate.

p-Dichlorobenzene, commercial, Paradow.

Nitric acid, C.P.

Gooch crucibles are used for filtration. The asbestos pad consists of a layer of medium fibers covered by a layer of fine fibers. It is ignited at 800° C for at least an hour.

PROCEDURE

Cut the rubber into small cubes and weigh out samples of 0.2 to 0.25 gram accurately. Place 20 grams of *p*-dichlorobenzene in a 125-cc. Erlenmeyer flask with ground-glass joint, fitted with a reflux condenser, or in a 150-cc. beaker, which may be covered by a 125-cc. Erlenmeyer flask filled with cold water. Heat on the hot plate until the *p*-dichlorobenzene is melted, add the rubber sample, and adjust the temperature of the hot plate so that the liquid boils gently. Softening for half an hour is sufficient in most cases. Cool the solution slightly (80° to 90° C), and add 5 cc. of *tert*-butyl hydroperoxide and 1 cc. of osmium tetroxide solution. Heat to about 120° C and keep there for 30 minutes. Cool the mixture to 50° to 60° C and add 25 cc. of reagent grade benzene. Filter through the Gooch crucible while still slightly warm. No difficulty is encountered in filtration; the carbon settles out readily and has no tendency to run through the filter. (In isolated cases, the addition of a few cc. of ether may serve to speed the filtration). Wash the filter and beaker with benzene; empty the filter flask, and wash the filter with two 5-cc. portions of warm nitic acid (1:2), using gentle suction. Wash with several portions of distilled water, dry the crucible at 325° to 350° C for 0.5 hour, cool in a desiccator, and weigh quickly. Ignite at 750° to 800° C, cool, and weigh. The loss in weight represents the carbon present in the original sample.

Calculate the per cent of free carbon from the expression:

$$\% \text{ free carbon} = \frac{\text{wt. of crucible and carbon} - \text{wt. of crucible after ignition}}{\text{wt. of sample}} \times 100$$

ANALYTICAL RESULTS

Four samples of carbon black, corresponding in weight to 25 to 30 per cent carbon black loadings of rubber samples 0.2 to 0.25 gram in weight, were run through the entire procedure. To two of the samples, sufficient GR-S was added to make the combined weight approximately 0.2 gram. It appears from the results given in Table I that no correction factor is necessary.

TABLE I

BLANK ANALYSES OF CARBON BLACK

Carbon black	Weight taken (gram)	Weight found (gram)
No rubber present		
Philblack-O (RF)	0.0390	0.0379
Sterling-99 (FF)	0.0622	0.0607
About 0.14 gram of GR-S present		
Spheron-6 (MPC)	0.0514	0.0501
Philblack-A (HMF)	0.0752	0.0746

Four specimens of cured rubber stock were analyzed by this procedure. The results of the analyses are given in Table II.

TABLE II

ANALYSES OF VULCANIZED RUBBER STOCKS

Type of rubber	Inorganic filler	Amt. of filler (%)	Nominal carbon black (%)	No. of detns.	Carbon found % (Av.)	Av. deviation of mean (% Abs.)
Natural	Zinc oxide	2	30.4	7	30.5	0.21
Neoprene	Magnesium oxide	2.6	23.6	5	23.9	0.21
Type GN	Zinc oxide	3.8				
Butyl	Zinc oxide	3.1	28.8	3	28.6	0.13
GR-S	Zinc oxide	1.9	28.2	5	28.3	0.20

The average deviation of a single determination never exceeded 0.6% absolute. The method appears sufficiently accurate to recommend it for control work on rubber-carbon black master batches.

SUMMARY

A method for the determination of free carbon in vulcanized rubber stocks is described. The sample is softened in boiling *p*-dichlorobenzene before treatment with *tert*-butyl hydroperoxide in the presence of osmium tetroxide. No difficulties are encountered in the filtration of the carbon black. The carbon black is washed on the filter with dilute nitric acid to remove acid-soluble inorganic fillers. The method has been successfully applied to natural rubber, GR-S, Butyl rubber, and Neoprene. No correction is necessary.

ACKNOWLEDGMENT

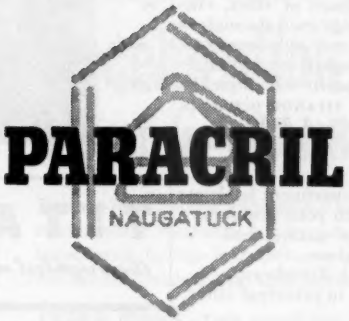
The authors are indebted to G. D. Louth of the Firestone Tire and Rubber Company, who furnished the certified stock, with information on the kind and amount of inorganic filler.

REFERENCES

[1] American Society for Testing Materials, "1946 Standards", Part III B, Specification D297-43T, p. 941; D833-46T, p. 976.
[2] McCready and Thompson, *Ind. Eng. Chem. Anal. Ed.* **18**, 522 (1946).
[3] Louth, *Anal. Chem.* **20**, 717 (1948).
[4] Barnes, Williams, Davis, and Giesecke, *Ind. Eng. Chem. Anal. Ed.* **16**, 9 (1944); Galloway and Wake, *Analyst* **71**, 505 (1946).
[5] Decker, *Chem. Weekblad* **39**, 624 (1942).
[6] Tyler and Higuchi, *India Rubber World* **116**, 635 (1947).
[7] Bauminger and Poulton, *Analyst* **74**, 351 (1949).
[8] Kolthoff, Lee and Carr, *J. Polymer Sci.* **1**, 429 (1946).

Announcement...

Naugatuck Chemical is now producing and distributing



An Acrylonitrile — Butadiene Polymer... outstanding for its resistance to oils and gasolines

PARACRIL B
General Purpose Oil Resistant Type
Excellent Heat Resistance.

PARACRIL-BJ
Same General use as "B" but lower plasticity and easier processing.

PARACRIL-C
Maximum Oil Resistance. Excellent heat resistance and aging properties.

Price list available upon request

Process · Accelerate · Protect
with
NAUGATUCK CHEMICALS

Naugatuck Chemical DIVISION OF UNITED STATES RUBBER COMPANY

NAUGATUCK, CONNECTICUT

IN CANADA: NAUGATUCK CHEMICALS DIVISION • Dominion Rubber Company Limited, Elmira, Ontario

RUBBER CHEMICALS · AROMATICS · SYNTHETIC RUBBER · PLASTICS · AGRICULTURAL CHEMICALS · RECLAIMED RUBBER · LATICES

TITANOX PIGMENTED

for Quick, Lasting Identification

... Full Electrical Protection

White and tinted insulations of latex, vinyl or polystyrene are greatly improved through the use of TITANOX-RA. It is not only compatible with these compounds but imparts exceptional whiteness or increased opacity which yields bright, clear tints. Furthermore, TITANOX pigments, because of their stability and dielectric characteristics, contribute to the electrical value of the insulation.

Our Technical Service Department is always available to help you with your problems in pigmenting all types of natural and synthetic polymers. Titanium Pigment Corporation, 111 Broadway, New York 6, N. Y. Offices in principal cities.

TITANOX

the brightest name in pigments

8847

TITANIUM PIGMENT CORPORATION

Subsidiary of NATIONAL LEAD COMPANY

ADVERTISE *in*

RUBBER CHEMISTRY AND TECHNOLOGY

KEEP YOUR NAME AND YOUR PRODUCTS CONSTANTLY BEFORE THE RUBBER TECHNOLOGIST

Advertising rates and information about available locations may be obtained from E. H. Krismann, Advertising Manager, Rubber Chemistry and Technology, care of E. I. du Pont de Nemours & Company, 40 East Buchtel Ave. at S. High St., Akron 8, Ohio.

Here's why

Du Pont THIONEX-MBTS Acceleration is best for "Cold Rubber" Treads

Thionex-MBTS acceleration gives you more for your money in cold rubber treads containing fine furnace blacks. Here are the advantages found by tire manufacturers in tests comparing Thionex-MBTS combinations with their regular-production accelerator.

TREAD WEAR—Tests proved that the treads of tires containing Thionex-MBTS combinations wore fully as well as the treads of the control tires.

TREAD CRACKING—Treads accelerated with Thionex-MBTS showed no evidence of crack growth during test runs as long as 43,000 miles.

PROCESSING SAFETY—Actual factory processing experience showed that stocks accelerated with Thionex-MBTS have little or no tendency to scorch. Mooney scorch times of about 30 minutes are typical of "cold rubber" tread compounds containing Thionex-MBTS accelerator.

STORAGE STABILITY—Unlike compounds containing some types of accelerators, stocks containing Thionex-MBTS acceleration do not lose curing strength nor do they "set up" even after prolonged storage.

COST—The use of Thionex-MBTS acceleration saved money . . . was 40-50% lower in cost than their regular-production accelerators.

● For complete information on Thionex-MBTS acceleration see Report BL-235 or ask your Du Pont representative. E. I. du Pont de Nemours & Co. (Inc.), Rubber Chemicals Division, Wilmington 98, Delaware.

DU PONT RUBBER CHEMICALS

E. I. du Pont de Nemours & Co. (Inc.), Wilmington 98, Del.

DU PONT

BETTER THINGS FOR BETTER LIVING . . . THROUGH CHEMISTRY

"Misfit"

formulations may be hiking your production cost

*There's one formulation—and only one—that will keep your manufacturing or processing costs at a minimum. Let UBS "Creative Chemistry" lower your costs and increase production efficiency by recommending formulations tailored to your specific requirements.

Our technical staff will be glad to consider your problems without obligation.

Serving industry with "creative chemistry"

Industrial Latex Adhesives
Rubber Solvent Cements
Synthetic Solvent Cements
Backing Compounds
Combining and Laminating Cements
Coating Compounds
Latex Concentrates
Tank Lining Compounds
Polystyrene Dispersions
Latex Extenders, Tackifiers

. . . Technical data sheets for each product available on request. *Write for yours today!*

Address all inquiries to the Union Bay State Chemical Company, 50 Harvard Street, Cambridge 42, Massachusetts.

UNION BAY STATE
Chemical Company

Serving Industry with Creative Chemistry
ORGANIC CHEMICALS · SYNTHETIC LATEX · SYNTHETIC RUBBER
PLASTICS · INDUSTRIAL ADHESIVES · DISPERSIONS
COATING COMPOUNDS · IMPREGNATING MATERIALS · CEMENTING CEMENTS

Material for ALL RUBBER and PLASTIC COMPOUNDING

COLORS

FILLERS

SOFTENERS

EXTENDERS

PLASTICIZERS

RESINS . . .
PARA-COUMARON INDENES
HYDRO-CARBON TERPENES
MODIFIED STYRENES
AROMATIC HYDRO-CARBONS

PRECISION Uniformity

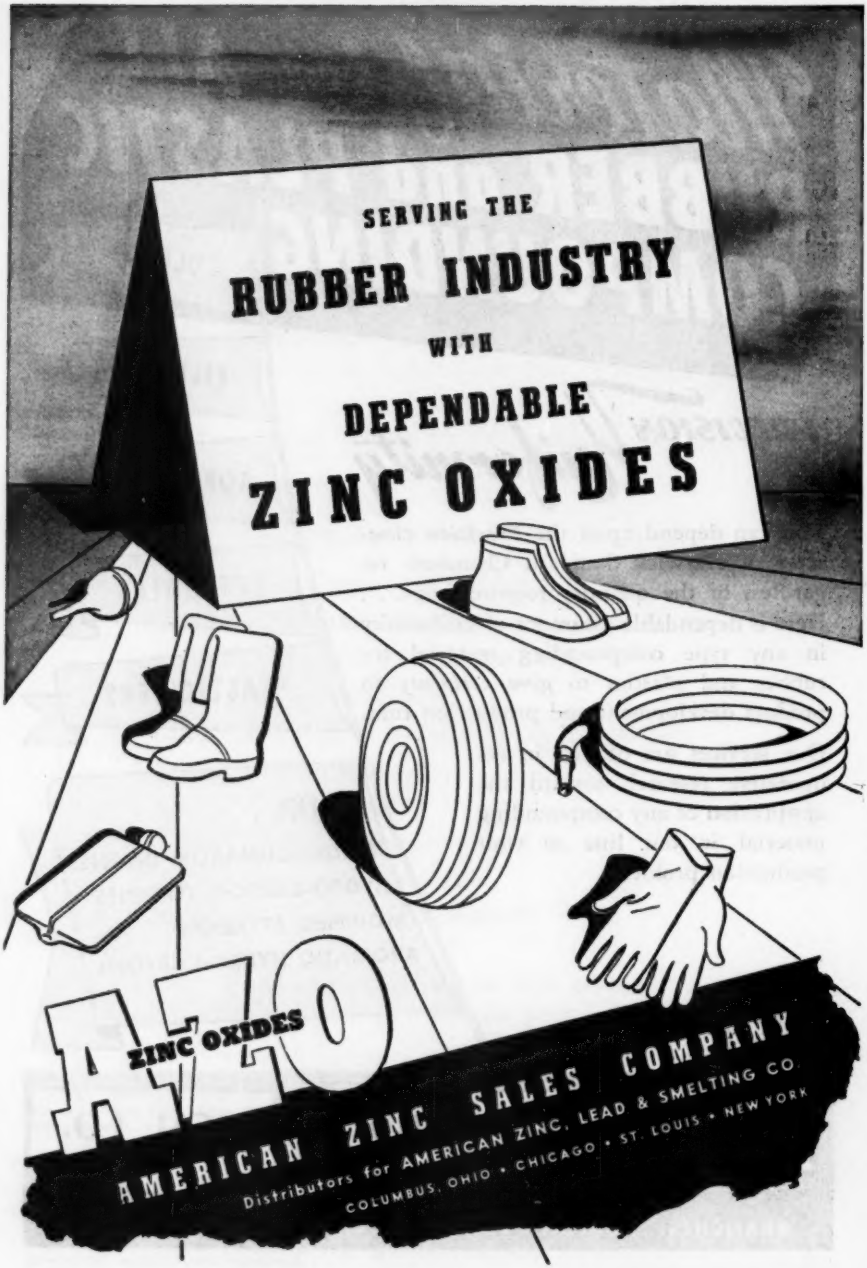
You can depend upon the *Precision* character of Harwick Standard Chemicals regardless of the quantity requirement . . . Here is dependable assurance of uniformity in any type compounding material for rubber and plastics to give *certainty* in product development and production runs.

Our services are offered in co-operative research toward the application of any compounding material in our line to your production problems.

HARWICK STANDARD CHEMICAL CO.

AKRON 5, OHIO

BRANCHES: BOSTON, TRENTON, CHICAGO, LOS ANGELES


SERVING THE
RUBBER INDUSTRY
WITH
DEPENDABLE
ZINC OXIDES
AZO
ZINC OXIDES
AMERICAN ZINC SALES COMPANY
Distributors for AMERICAN ZINC, LEAD & SMELTING CO.
COLUMBUS, OHIO • CHICAGO • ST. LOUIS • NEW YORK

The C.P. Hall Co.
CHEMICAL MANUFACTURERS

ACCELERATORS
PLASTICIZERS
ANTIOXIDANTS

A Complete Line of Approved Compounding Materials

● AKRON, OHIO • LOS ANGELES, CALIF. • CHICAGO, ILL. • NEWARK, N. J.

STAMFORD "FACTICE" VULCANIZED OIL

(Reg. U. S. Pat. Off.)

Our products are engineered to fill every need in natural and synthetic rubber compounding wherever the use of vulcanized oil is indicated.

We point with pride not only to a complete line of solid Brown, White, "Neophax" and "Amberex" grades, but also to our aqueous dispersions and hydrocarbon solutions of "Factice" for use in their appropriate compounds.

Continuing research and development in our laboratory and rigid production control has made us the leader in this field.

The services of our laboratory are at your disposal in solving your compounding problems.

THE STAMFORD RUBBER SUPPLY COMPANY

STAMFORD, CONNECTICUT

Manufacturers of "Factice" Brand Vulcanized Oil
Since 1900

now available

to Purchasing Agents and Technologists in the ZnO-consuming industries — *with our compliments*

As the table of contents* indicates, this [illegible]ive page book is intended to be a complete and informative manual on lead-free zinc oxide. In preparing the book, we have included only that material which we considered to be of maximum interest and value to technologists in the consuming industries.

The book has been divided into two parts. Section I concerns itself with the production of St. Joe commercially lead-free zinc oxides; it is a detailed and illustrated, step-by-step itinerary which begins underground in one of our zinc mines in upper New York State, and ends with the packing of the finished product in our Josephtown, Pennsylvania plant. Section II contains representative technical data on our various grades of black, red and green label zinc oxides, accompanied by photomicrographs and charts analyzing their particle size distribution characteristics. In addition, Section II includes a brief discussion of the role of zinc oxide in the major consuming industries.

Our reason for devoting twenty pages of this book to the production aspects of our zinc oxides will become apparent upon consideration of these facts: The trade term "Zinc Oxide" describes a series of materials that may be quite different from the material which is identified by the chemical symbol ZnO. Actually, ZnO is only a part of the materials thus described although its content is usually from 95.0 to 99.8% by weight. Other materials which may be a component part of commercial zinc oxides are, in some cases, beneficial and in others objectionable from the viewpoint of the consumer as well as the manufacturer.

Generally speaking, the characteristics possessed by the various zinc oxides now on the market were not developed by specifications set up by consumers, *but are the result of the various conditions surrounding the manufacture of the pigments.* A knowledge of zinc oxide production is thus an asset to consumers because different production methods result in pigments possessing different chemical or physical properties, and their applications have certain limitations which are important for consumers to recognize. This is the reason we have covered our production methods in considerable detail, and it is our belief that this will result not only in a better and wider utilization of commercially lead-free zinc oxides generally, but also in a greater appreciation of the high quality of St. Joe Zinc Oxides.

*** CONTENTS**

- A Short History of the St. Joseph Lead Company
- The Production of St. Joe Zinc Oxides
- General Properties of Zinc Oxide
- Zinc Oxide in Rubber Compounds
- St. Joe Rubber Grade Zinc Oxides
- Zinc Oxide in Protective Coatings
- St. Joe Paint Grade Zinc Oxides
- Zinc Oxide in the Chemical, Pharmaceutical and Other Industries
- Zinc Oxide in the Ceramic Industries
- St. Joe Ceramic Grade Zinc Oxides

PLEASE WRITE FOR YOUR COPY ON YOUR COMPANY LETTERHEAD

ST. JOSEPH LEAD COMPANY

250 PARK AVENUE, NEW YORK 17 • PRODUCERS OF LEAD-FREE ZINC OXIDES

For Prompt and Complete Coverage of Current Technical and News Developments in the Rubber Industry—

READ

RUBBER AGE

One of the World's Outstanding Rubber Journals

$3.00 a year

★

For Full Information on Rubber Manufacturers and Their Products; Material, Equipment and Services Used by Rubber Manufacturers; Who's Who in the Rubber Industry—

READ

Rubber RED BOOK

Directory of the Rubber Industry

1951 Edition Available in June, 1951

$7.50 a copy

Published By

PALMERTON PUBLISHING COMPANY, Inc.

250 West 57th Street New York 19, N. Y.

TESTED IS TRUSTED

3 Styles Available

1) MODEL E, self contained unit with electric stirrer, control panel, insulated cold tank of stainless steel, as illustrated above. Conforms to ASTM Designation D746.
2) For application to a standard T-50 *Scott Tester (Type A, ASTM Specification D599-40T) apparatus.
3) For installation in existing cold box equipment.

At 3 prices — REQUEST DETAILS

Registered **SCOTT TESTERS** Trademark

SCOTT TESTERS, INC. 102 Blackstone St. Providence, R. I.

Scott Testers — Standard of the World

A *MUST* for every COMPOUNDER OF RUBBER

1947 Second Edition

COMPOUNDING INGREDIENTS FOR RUBBER

The new book presents information on some 2000 separate products as compared to less than 500 in the first edition, with regard to their composition, properties, functions, and suppliers, as used in the present-day compounding of natural and synthetic rubbers. There is also included similar information on natural, synthetic, and reclaimed rubbers as the essential basic raw materials.

Over 600 pages—Cloth Bound
Price $5.00 postpaid in U.S.A.
$6.00 Foreign
(Add 2% Sales Tax for New York City)

INDIA
RUBBER WORLD
386 FOURTH AVENUE NEW YORK 16, N. Y.

RUBBER SUBSTITUTES

(Vulcanized Vegetable Oils)

◆

Manufactured since 1903 by

THE CARTER BELL MFG. CO.

SPRINGFIELD NEW JERSEY

Represented by:

HARWICK STANDARD CHEMICAL CO.

Akron — Boston — Trenton — Chicago — Denver — Los Angeles

HI-SIL SILENE EF in GR-S

get these facts NOW

on changing-over
from natural rubber compounds to GR-S
—to prepare for increased restrictions

Write for these free COLUMBIA PIGMENT DATA SHEETS

No. 50-10. Acceleration of Hi-Sil Compounds with Thiazole-Guanidine Combinations.

No. 50-3. Compounding of Low Temperature GR-S with a New Fine Particle Silica.

Compounding of GR-S with a New Fine Particle Silica. (India Rubber World, August, 1949.)

No. 47-7. Silene EF and Calcene T in GR-S 10.

No. 47-4. Comparison of Mixtures of Calcene T and Silene EF with other Fine Calcium Carbonates in GR-S at Medium and High Loadings.

No. 47-1. General Compounding Data of Silene EF and GR-S Formulations.

No. 45-1. The effect of Varying Quantities of Ethylene Glycol on the Properties of GR-S Stocks Containing Silene EF.

COLUMBIA CHEMICALS

PAINT • GLASS • CHEMICALS • BRUSHES • PLASTICS

PITTSBURGH PLATE GLASS COMPANY

WHITETEX

A new white and bright pigment for rubber, synthetic rubber or plastics, especially vinyls.

BUCA

A proved pigment for compounding ALL types of natural and synthetic rubber.

CATALPO

For compounding rubber and synthetic rubber.

No. 33 CLAY

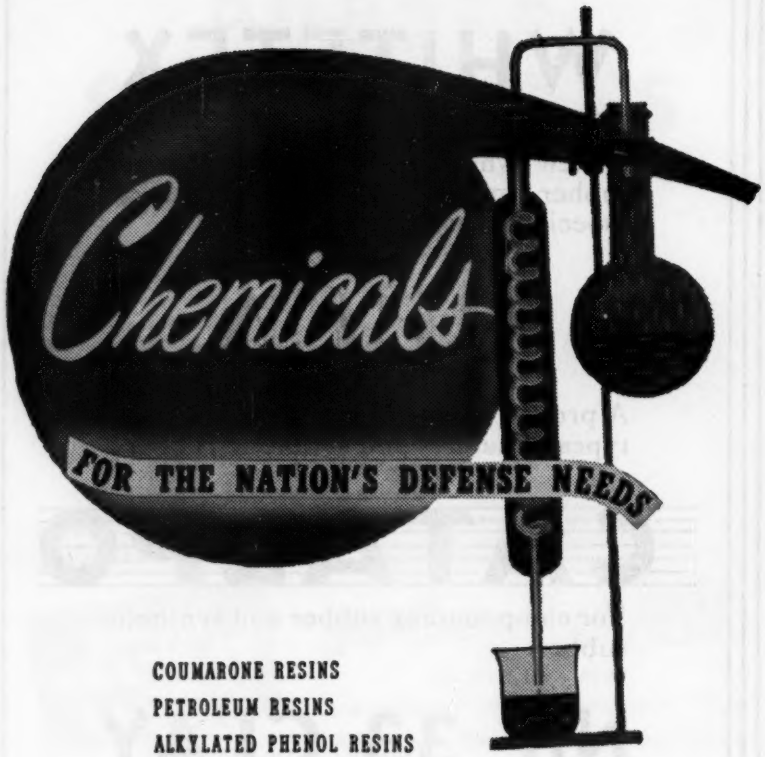
For wire and vinyl compounding.

For full details, write our Technical Service Dept.

SOUTHERN CLAYS, INC.

(Formerly P. W. Martin Gordon Clays, Inc.)

33 Rector Street · New York 6, N.Y.



COUMARONE RESINS
PETROLEUM RESINS
ALKYLATED PHENOL RESINS
PLASTICIZING OILS
COAL-TAR SOLVENTS AND OILS
NEUTRAL AND SHINGLE STAIN OILS
RUBBER RECLAIMING OILS
CHEMICAL SPECIALTIES

THE NEVILLE COMPANY NEVILLE PITTSBURGH 25, PA.

Plants at Neville Island, Pa., and Anaheim, Cal. A39

STOP RISING COSTS

with

Piccolyte

the versatile resin

Costs Less...Offers More!

Piccolyte—a pure hydrocarbon, thermoplastic terpene resin—is low in cost and readily soluble in low-cost naphthas, pentane and hexane. It is pale and stable in color, chemically inert, compatible with many other materials, non-toxic. There are nine melting points.

Piccolyte has the same carbon to hydrogen ratio as plantation rubber, and has excellent tack-producing properties. Ideal for rubber tile and other products where light colors and tints are demanded.

Use Piccolyte to keep your costs down without sacrificing in any way the quality of your products. Piccolyte costs less per pound today than practically all other resins, yet offers the maximum in quality and service.

Write for data booklet, and a free sample of PICCOLYTE. Give intended use, so we can send sample of appropriate grade.

PENNSYLVANIA
INDUSTRIAL CHEMICAL CORP.
CLAIRTON, PA.

Plants at Clairton, Pa. and Chester, Pa.
Distributed by Harwick Standard Chemical Co., Akron 5, Ohio

ANTIMONY SULPHIDE

Regular Grades *for* Attractive Color

Also

A special grade for obtaining colored stocks having high abrasion resistance

RARE METAL PRODUCTS CO. **ATGLEN, PENNA.**

To the

Rubber Industry! ~ ~ ~

This Journal is supported by advertising from leading suppliers to the industry. More advertising will permit the publication of a greater number of important technical papers on rubber which will make RUBBER CHEMISTRY AND TECHNOLOGY even more valuable as a convenient reference of "Rubberana."

Specify materials from suppliers listed on page 32. Urge other suppliers to adverstise in

RUBBER CHEMISTRY AND TECHNOLOGY

●

Advertising rates and information about available locations may be obtained from E. H. Krismann, Advertising Manager, Rubber Chemistry and Technology, c/o E. I. du Pont de Nemours & Company, 40 E. Buchtel Ave. at High Street, Akron 8, Ohio.

THE VANDERBILT MODEL LABORATORY

NORWALK, CONNECTICUT

Here we learn how our materials can be used by our customers to their best advantage. We invite and appreciate your cooperation.

Please feel free to visit our laboratory, to discuss your problems with us and to use our facilities to work them out if you care to do so.

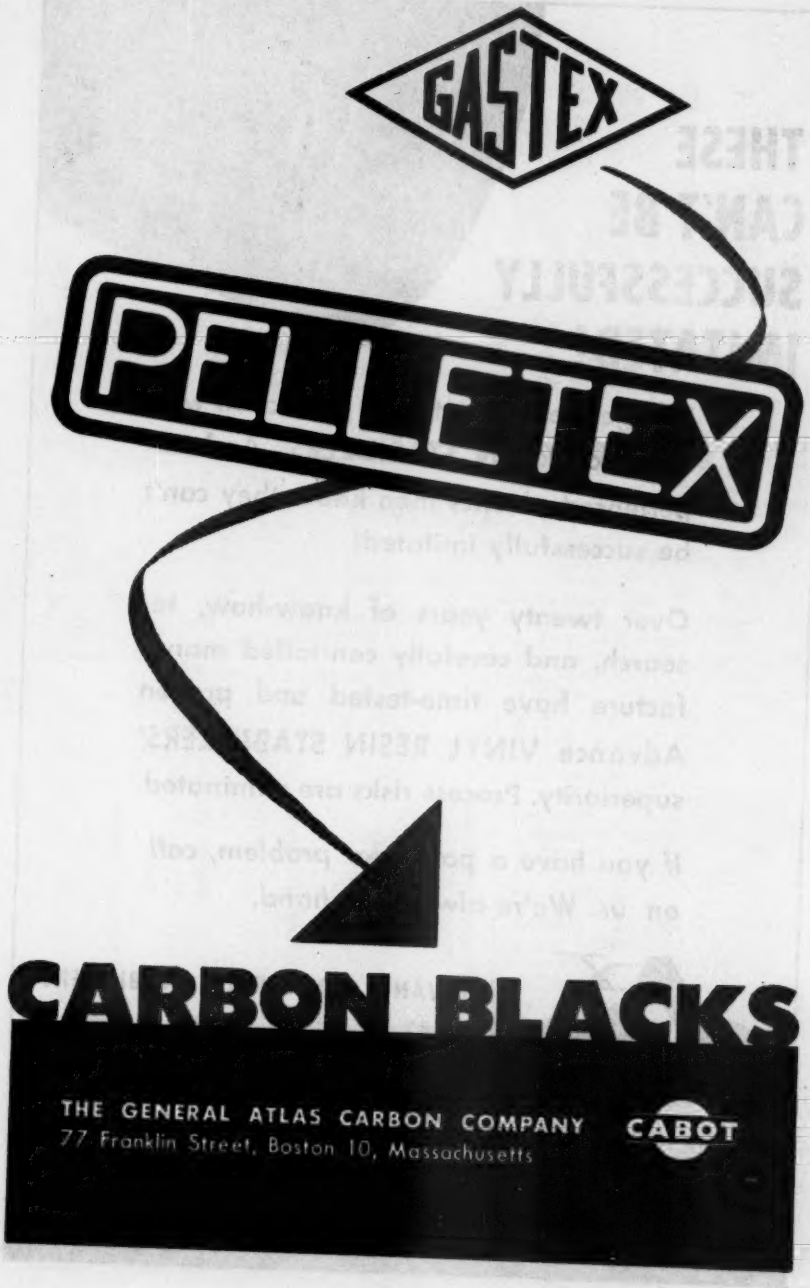
R. T. VANDERBILT CO., INC.

230 Park Avenue, New York City

RUBBER CHEMISTRY AND TECHNOLOGY IS SUPPORTED BY ADVERTISING FROM THESE LEADING SUPPLIERS

INDEX TO ADVERTISERS

	Page
Advance Solvents & Chemical Corp. (Opposite Inside Back Cover)	34
American Cyanamid Company, Calco Chemical Division	11
American Zinc Sales Company	20
Barrett Div., The, Allied Chemical & Dye Corp. (Inside Back Cover)	
Binney & Smith Company (Opposite Table of Contents)	14
Cabot, Godfrey L., Inc.	9
Carter Bell Manufacturing Company, The	26
Du Pont Rubber Chemicals Division	17
General Atlas Carbon Company	33
Goodyear Tire & Rubber Company, The	5
Hall, C. P. Company, The	21
Harwick Standard Chemical Company	19
India Rubber World	25
Monsanto Chemical Company	8
Naugatuck Chemical Division (U. S. Rubber Company)	15
Neville Company, The	28
New Jersey Zinc Company, The (Outside Back Cover)	
Pan-American Refining Corp., Pan American Chemicals Div.	10
Pennsylvania Industrial Chemical Corporation	29
Phillips Chemical Company	2
Pittsburgh Plate Glass Company, Columbia Chemical Div.	26
Rare Metal Products Company	30
Richardson, Sid Carbon Company	7
Rubber Age, The	23
St. Joseph Lead Company	22
Scott Testers, Inc.	24
Sharples Chemicals, Inc.	3
Southern Clays, Inc.	27
Stamford Rubber Supply Company, The	21
Sun Oil Company, Sun Petroleum Products (Opposite Title Page)	12
Thiokol Corporation, The	4
Titanium Pigment Corporation	16
Union Bay State Chemical Company	18
United Carbon Company (Inside Front Cover)	
Vanderbilt, R. T. Company	31
Witco Chemical Company (Opposite Inside Front Cover)	1
Wyandotte Chemicals Corporation	6


GASTEX
PELLETEX
CARBON BLACKS
THE GENERAL ATLAS CARBON COMPANY
77 Franklin Street, Boston 10, Massachusetts
CABOT

THESE CAN'T BE SUCCESSFULLY IMITATED!

You get better heat-light protection with Advance RESIN STABILIZERS. And experienced plastics men know they can't be successfully imitated!

Over twenty years of know-how, research, and carefully controlled manufacture have time-tested and proven Advance VINYL RESIN STABILIZERS' superiority. Process risks are eliminated.

If you have a particular problem, call on us. We're always on hand.

Advance

Write for Literature

ADVANCE VINYL RESIN STABILIZERS

#3	#52	#21	E6B
V-1-N	JCX	VL-3	BC-12

OTHERS PREPARED TO FIT YOUR NEEDS

ADVANCE SOLVENTS & CHEMICAL CORP.

245 Fifth Avenue · New York 16, N. Y.

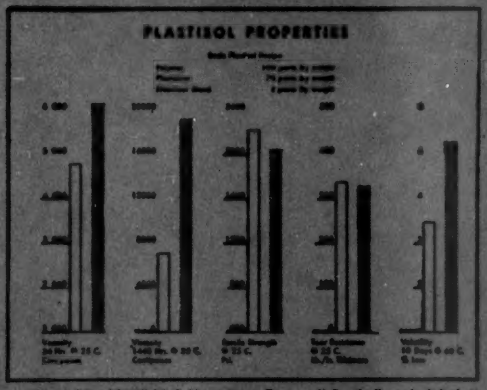
HOW TO GET

IMPROVED QUALITY AND LOWER VISCOSITY PLASTISOLS WITH BARRETT* ELASTEX* 10-P PLASTICIZER

In the manufacture of plastisols for coating and low-pressure molding operations, compounders have long known the value of di-2-ethylhexyl phthalate as a primary plasticizer. Dispersions of vinyl resins in this plasticizer possess good storage stability, and are of moderately low viscosity. The coatings and molded articles produced from them exhibit good physical and performance characteristics.

Now Barrett offers the plastisol compounder an even more efficient dispersant—"ELASTEX" 10-P Plasticizer. Plastisols prepared with this high-quality primary plasticizer possess lower viscosity and better storage stability than do those compounded with equivalent amounts of di-2-ethylhexyl phthalate. At the same time, the fused products exhibit improved physical properties, and are subject to less volatile loss.

If you manufacture plastisols for spread coating, molding, or casting, the superior performance of Barrett "ELASTEX" 10-P Plasticizer is well worth investigating.



Key: Black "ELASTEX" 10-P Plasticizer; Grey—di-2 ethylhexyl phthalate

✓ NOTE: Technical advice on the use of BARRETT Chemicals is available to you through the assistance of Barrett representatives. Why not put your problem up to us? Phone, wire or write.

BARRETT* CHEMICALS AVAILABLE TO THE PLASTICS INDUSTRY

"ELASTEX" 10-P Plasticizer	"ELASTEX" DCHP Plasticizer	Phthalic Anhydride
"ELASTEX" 28-P Plasticizer		Phenol
"ELASTEX" 50-B* Plasticizer	Dibutyl Phthalate	Crystal Urea

Barrett®

*Reg. U. S. Pat. Off.

THE BARRETT DIVISION

ALLIED CHEMICAL & DYE CORPORATION

40 Rector Street, New York 6, N. Y.

In Canada: The Barrett Company, Ltd., 5551 St. Hubert Street, Montreal, Que.

You can formulate *FASTER... BETTER* with

HORSE HEAD® ZINC OXIDES

[redacted]

...Because the Horse Head line comprises the most complete family of Zinc Oxides for rubber:

1. It is the only line having such a wide range of particle sizes, surface conditions and chemical compositions.
2. Its *conventional* types cover the range of American and French Process oxides.
3. Its *exclusive* types include the well-known Kadox and Protox brands.

That means you need not waste time adapting a single Zinc Oxide to each specific compound. Instead, just choose from the Horse Head line the Zinc Oxides that best meet your needs.

[redacted]

...Because you need to compromise less when you choose from the wide variety of Horse Head Zinc Oxides.

...Because the Horse Head brands can improve the properties of your compounds.

Year after year, for nearly a century, more rubber manufacturers have used more tons of Horse Head Zinc Oxides than of any other brands.

THE NEW JERSEY ZINC COMPANY

Founded 1848

160 Front Street, New York 7, N. Y.